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OF THE
AMERICAN INSTITUTE OF MI
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(INCORPORATED)

Volume 159

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OF NONFERROUS META
1944

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FOREWORD

NOT since 1936 has the Institute published a volume of TRANSACTIONS devoted to that important branch of metallurgy that includes the reduction of ores and concentrates and the refining of the metals thus produced. In that year appeared a 740-page volume on the Metallurgy of Lead and Zinc, sponsored by the technical committee headed by Carle R. Hayward. Three years earlier, the Committee on Reduction and Refining of Copper, of which Charles R. Kuzell was chairman, sponsored a volume of almost exactly the same size on Copper Metallurgy. These were extremely comprehensive volumes that in each field brought the state of the art well up to date and evoked high commendation. Technologic progress, of course, has continued since those volumes appeared; but for reasons beyond their control the flow of significant technical articles on copper, lead, and zinc has been limited despite the efforts of the following able chairmen: Copper—C. W. Eichrodt, E. R. Marble, E. W. Rouse, P. D. I. Honeyman, A. E. Wheeler, and Curtis L. Wilson; Lead and Zinc—E. P. Fleming, Herbert R. Hanley, and Arthur A. Center.

The present volume represents a departure in that it deals with (1) the ferroalloying, (2) the lightweight, and (3) the so-called "minor" metals, in addition to the trio of "major" nonferrous metals. The published technical literature on the production of the first two of these groups has been extremely meager in the past. Moreover, the preoccupation of potential authors with war work, restrictions imposed by military censorship, and in some cases reticence arising from a desire to avoid patent complications, has prevented the contribution of many papers that would have added to the value of the volume.

Despite these handicaps, Philip D. Wilson, who undertook the chairmanship of a new Committee on Reduction and Refining of Aluminum and Magnesium in 1943, has been able to obtain an excellent group of papers dealing with these two light metals and is particularly to be commended. Dr. Gilbert Seil, Chairman of the new Committee on Reduction of Ferroalloy Ores, was somewhat less fortunate, but this was not because of any lack of willingness and

FOREWORD

diligence on his part. Circumstances and custom conspired against him. Perhaps the time will come when the publication of papers on the techniques in this important field will be more generous than it has been.

Even though the volume is not as well balanced as had been hoped, the profession is deeply indebted to the chairmen and members of the sponsoring committees and to the authors who willingly contributed their time and talent.

A. B. PARSONS,
Secretary, A.I.M.E.

NEW YORK, N. Y.
November 1, 1944.

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Changes and Improvements in Modern Copper Smelting

BY R. A. WAGSTAFF,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

SINCE the time of the early Egyptians, the use of copper has been a boon to the life of most of the civilized world. Its use has been varied; in many connections, the art by which it attained its greatest usefulness has been lost.

In this paper an endeavor will be made to take into consideration some of the many changes that have occurred during the last 40 years of copper-smelting operations. During that period the copper blast furnace has been almost forced out of existence by new methods of ore concentration—first, gravity concentration, and then flotation.

These new methods of concentration introduced many new factors into the metallurgy of copper. The product was wet, it was fine and it was high grade. To overcome all these factors many changes have been necessary throughout the smelting agenda.

New equipment has been necessary for transportation, unloading, sampling, bedding and moisturing in all smelting plants, especially the custom smelter. During the early days of "flotation," little was known about filtering or the use of an alkaline circuit; often the concentrate going to the smelter contained 20 to 25 per cent moisture. It is easy to imagine the difficulty arising with a product of this nature when it had to be shoveled by hand labor. To meet these conditions, mechanical unload-

ing and sampling devices were soon developed. In many instances such good progress was made that actual costs for handling this unfavorable product were lower than those formerly incurred on the old product.

Today most sampling of copper ores and concentrates is being done by mechanical sampling, pipe or augur sampling, or shovel sampling. Where concentrates are uniform in metal content, a great many of the plants now use pipe or augur sampling. For spotty ores, the old shovel sample with cone and quartering during the final stages is still in use. Where big tonnages are handled, mechanical sampling of concentrates is being done, with satisfactory results. To curtail slow and tedious cutting and mixing procedure, mechanical mixing boxes, splitters and cutters are used to cut down labor costs.

MILLING

As crude ores become scarcer, the use of milling operations increases. The few crude ores that are still smelted are used as fluxing types. To use these ores finer grinding has been found advantageous. This has made for better bedding and fluxing conditions, which in turn makes for faster smelting, lower fuel consumption and better metal recovery. The degree of fineness is more or less determined by the nature of the product. Most plants have set a standard of through $\frac{3}{8}$ -in. mesh screen for roaster-reverberatory smelting and through $\frac{3}{4}$ -in. mesh screen for converter fluxes. For some refractory ores, even finer grinding has been found to be advantageous for good reverberatory smelting.

This paper was presented at a meeting of the Utah Section in 1943. Manuscript received at the office of the Institute Oct. 18, 1943. Issued as T.P. 1669 in METALS TECHNOLOGY, February 1944.

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ROASTING

The term "roasting of ores" is more or less a misnomer when considered in the light of past practice. Since the increased copper content of the charge means less elimination of sulphur, the various types of roasters are now putting through tonnages as high as 250 to 300 tons per day with an elimination of 6 to 8 units of sulphur. Considerable quantities of fuel are required in this type of roasting, as it is quite essential to have calcines as hot as possible for good smelting practice. To handle these large tonnages, all roaster equipment has undergone changes in construction and motive power.

There has been little or no change in actual roaster design, most plants using six to eight hearth roasters with a diameter of from 19 to 25 ft. Changes have been made in rabble design; some plants are using various types of abrasive resisting material as inserts in the wearing surface of the rabble blades, with considerable success. Air cooling is used in columns and arms instead of water. Considerable variation in arm speed is practiced, varying from one revolution per minute to one in 26 sec., a great deal depending on the type of charge. Where heavy elimination of sulphur is still required, drop-hole areas have been enlarged to allow faster elimination and less production of flue dust. Most roasters are now insulated with rock wool or infusorial earth, to conserve heat.

CHANGES IN SMELTING OPERATIONS

The real changes in copper smelting have been made in the actual smelting operations. Two lines of procedure are now being followed: (1) roasting and smelting, (2) direct smelting.

During the first 20 years of the century roasting and reverberatory smelting supplanted blast-furnace smelting. Two methods of reverberatory smelting have

been used. First, deep-bath center-drop smelting was the vogue, but as the charge changed from a coarse, granular product to the fine, high-grade concentrate, dust losses increased and high iron content caused rapid fluxing of furnace brickwork, it soon became apparent that changes would have to be made to offset these unfavorable factors. The answer was found in side feeding, which not only reduced dusting but also protected furnace side walls.

During these changes many efforts were made to increase the size of reverberatory furnaces to get larger tonnages, but little progress was made until it was found that these furnaces could not be made to smelt more material unless more fuel could be satisfactorily burned. This meant that exit areas for gases had to be made larger. The stress for copper and increased tonnage came as a result of the first world war and with this demand came the enlarged furnace uptakes. During the early days of the twentieth century, length of furnace was thought to be the best way to get more furnace area and larger tonnages, but soon this was found not to be so; closer studies proved that increased width gave much more satisfactory results. Furnaces are now being built just as wide as buckstays support will permit. One Canadian smelter using suspended arch construction has gone to a width of 35 ft. in the smelting zone. Furnace length is now governed by charging conditions, most plants endeavoring to keep unsmelted charge away from the skimming bay.

Little or no progress was made in reverberatory smelting during the early 1920's. This lull was caused by the Carson case, which involved most of the large copper-smelting plants. Just as soon as this was settled, two new smelting ideas were brought forth, the first being direct smelting and the second gun-feed deep-bath smelting.

Direct Smelting

Direct smelting of copper ores and concentrates was introduced in Mexico in an

to offset the increased costs of fuel version of a lower grade matte int

Today many plants in Africa United States have adopted this

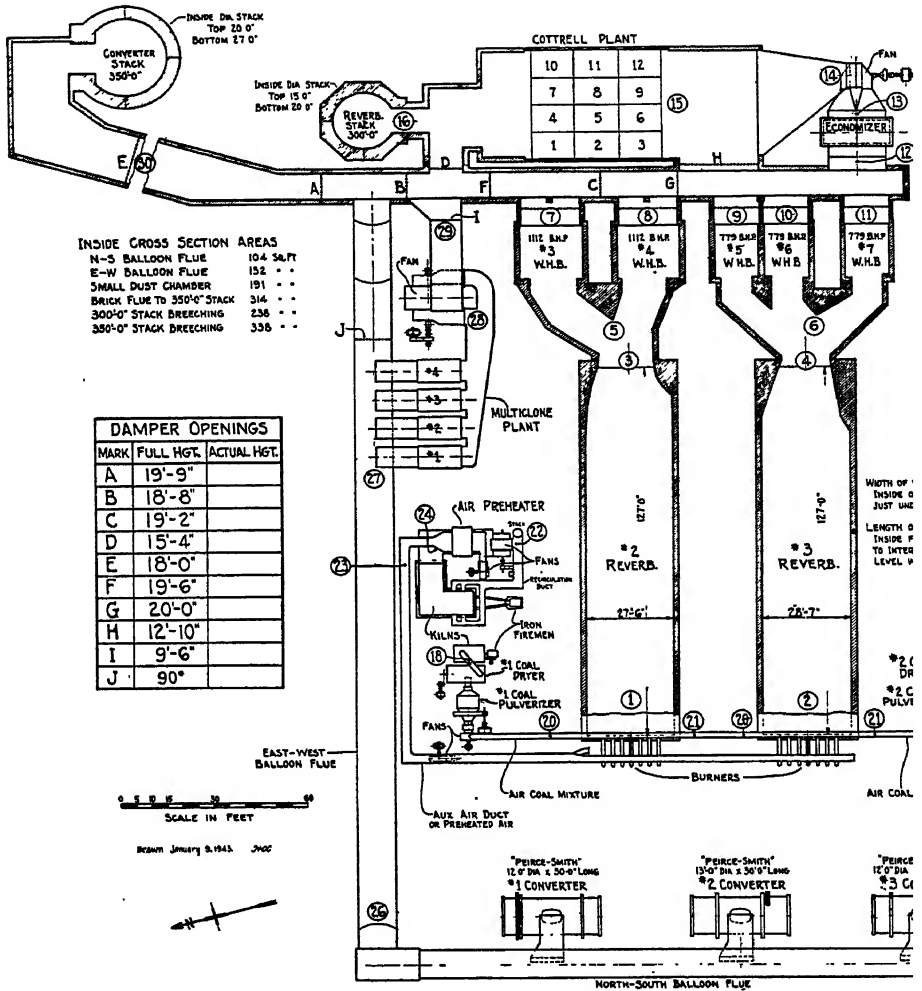


FIG. 1.—GAS FLOWSHEET, MCGILL SMELTER, NEVADA DIVISION OF KENNECOTT COPPER CORPORATION.

effort to get away from heavy flue dust and slag losses and to realize the use of excess fuel by waste-heat recovery. This method of smelting called for the elimination of all roasting equipment and it was hoped to avoid the necessity of Cottrell plant installation and thus save enough

smelting. Most of them are new been rebuilt during the last 10 years factors govern the choice of the smelting:

1. Less capital required for construction costs.

2. Requirements for power make possible the utilization of all excess fuel.

3. Sulphur content of charge allows the formation of an economical grade of matte.

The McGill smelting plant of the Nevada Mines Division, Kennecott Copper Corporation, seems to have been able to push direct smelting farther than any other organization. By changing furnace design, this plant has been able to increase the fueling rate from 125 tons of coal per day to 230 tons and smelt as high as 986 tons of solid charge per furnace day. Waste-heat boilers are larger than formerly, and thus recover 50 to 55 per cent of the heat released from the fuel burned. While fuel required per ton of charge has been high (6.376 million B.t.u. per ton of charge) the increase in tonnage no doubt has paid for itself.

Charging

Since all plants are not blessed with high-copper and low-sulphur charges, roasting and smelting operations still have a place in copper smelting. Two types of charging are being followed: (1) side-charging, (2) gun-feed, deep-bath smelting.

Side-charging reverberatory furnaces are used by all Canadian plants, Anaconda and some plants in Arizona. Many improvements have been made in construction, exit areas for gases are much larger and combustion areas in the smelting zone have been increased, to allow for greater consumption of fuel. Ribbed arch construction has been perfected to a point where furnace life is now a matter of months instead of days. During recent years, in Canadian plants, suspended arch construction has permitted the use of magnesite brick and has been very effective where the charge has been of a basic nature, but as the cost of magnesite brick is about four times that of silica brick, very few of the United States smelters have found it economical.

Deep-bath Smelting

Deep-bath smelting has attracted many operators, but, owing to the method of feeding, has given considerable trouble, both in metal losses and in erosion of brickwork caused by fluxing action of the dust in charging. To overcome these difficulties, the Garfield plant of the American Smelting and Refining Co. introduced the gun feed about 1928 in conjunction with deep-bath smelting. This method of charging showed very good possibilities and today is used on 12 furnaces in five different plants. The main features of this type of charging are: (1) better control of furnace-charging conditions, (2) less flue-dust loss (40 per cent), (3) better combustion areas in smaller furnaces, (4) better heat release from matte bath, (5) larger matte reservoir, (6) cleaner slags.

LIFE AND OPERATION OF PLANTS

During the past few years some very interesting papers have been written on the various plants. A comparison of some of the data gives a picture of what these

TABLE 1.—*Comparison of Data, Year 1940*

Type Smelting	Name of Plant	Tons Solid Charge Smelted per Fce. Day	Mil-lion B.t.u. per Solid Ton	H ₂ O Evapo-rated per Million B.t.u., Lb.
Direct side feed.	McGill	986	6.376	430
Calcine side feed	Noranda	1491	2.790	No figure
Calcine gun feed				
deep bath....	Clarkdale	1450	2.730	424

plants are doing (Table 1). Recent data from these plants shows that even better results have been obtained during 1941.

These large increases in tonnage smelted per furnace day have made the problem of furnace life very important. This problem is being met in different ways by the different plants; some of the better known schemes are as follows: (1) silica slurry,

junction with magnesite brick, (3) slotted arch construction, (4) ribbed arch construction, (5) water-cooled copper sidewall jackets (deep-bath smelting).

longer without a major arch repair. Clarkdale reports a furnace that has been in the stack since June 27, 1939, having smelted more than 1,300,000 tons of charge. These



FIG. 2.—APPLICATION OF SILICA SLURRY, CLARKDALE SMELTER, PHELPS DODGE CORPORATION

The method used seems to be more or less a plant problem. Both silica-slurry patching and suspended magnesite arches have given satisfactory results. Where they have been used, more than a million tons of charge have been smelted before a major repair job was required. This type of furnace repair is being done at a cost of from four to six cents per ton of solid charge smelted.

Silica-slurry patching has been in use about four years. Considerable improvement in method of application and make-up of slurry has been made in recent months. About 3 per cent bentonite is found to be very beneficial and helpful in making a mixture that will adhere to brickwork. Some very remarkable furnace campaigns have been made in recent years. A furnace at the Hayden plant has now passed 1000-day life and is expected to last 60 days

figures seem incredible when compared with former figures of 90 to 100 days and 75,000 to 100,000 tons of charge per furnace campaign.

Some experimental work has been done with insulating materials. The greatest success has been noticed in plants where furnace tonnages have been low. These plants claim a saving of 10 per cent in fuel.

The use of water-cooled jackets along the bath line of deep-bath smelting furnaces is becoming standard practice. Every known type of refractory acid, basic and neutral, has been tried, with little or no success. When furnace tonnages are stepped up above 1200 tons per furnace day, the cost of side-wall repairs becomes a very important item. In most plants copper jackets with 1½-in. water coils have proved most satisfactory.

Ever since reverberatory furnaces have been used as smelting units, one of the important problems for the copper metallurgist has been a permanent furnace

FUEL

One of the main problems in good smelting practice has been the efficient burning



FIG. 3.—REVERBERATORY FURNACE OF HUDSON BAY MINING AND SMELTING COMPANY, SHOWING SUSPENDED ARCH.

bottom. Early practice was to put in a silica bottom and then carefully smelt this in place, with the hope that the highly infusible mass would serve as an impervious layer to the metal bath. Usually, owing to expansion and inability to make a homogeneous mass, these bottoms floated out after a short time. In recent years other schemes have been tried; the latest is the use of magnetite sand instead of silica. This material has a much higher specific gravity and a lower coefficient of expansion. Just what the metal-absorption properties will be is an unproved factor, but we do know that they will be no worse than a silica bottom that has been floated out.

of fuel. Ores today are being smelted by oil, coal and gas. Most plants are familiar with oil or coal as a fuel, but not until about 10 years ago was natural gas used as a fuel.

Combustion problems have been fairly well worked out for both oil and coal. Good burner equipment is now being used with efficient control equipment. Automatic control of draft, air and fuel supply have been so well synchronized that it is now almost impossible to get furnace combustion out of line.

Owing to the newness of natural gas, there will remain a number of problems to be solved. Combustion areas and proper

atomization of gas and air are still fields for research. Results to date have shown that natural gas as a fuel is 8 to 10 per cent less efficient than either oil or coal. One of the main drawbacks has been the inability to obtain a comparative tonnage per furnace day.

Most plants at first burned natural gas with the aspirating single-spud type of burner, which is very noisy and hard to regulate. High gas velocity also causes heavy turbulence, which makes for rapid deterioration of furnace brickwork. A great many plants have now installed multijet burners, which are less noisy and allow the gas to enter the furnace at much lower velocities. Furnace life has been lengthened by this type of burner, with no loss of efficiency. Experiments are now being carried on with forced-draft burners, in the hope of having a more flexible burner, which, in the long run, will give larger tonnages and better fuel ratios.

To date no real tests have been made on the preheating of air for combustion in reverberatory furnaces for copper smelting. Two plants are now getting ready to do some real experimental work; namely, the McGill smelter and the Chino smelter.

The McGill plant will try preheated air with coal and the Chino plant will try preheated air with natural gas. Both plants intend to use extraneous heat, with the idea of raising the furnace temperature within the smelting zone and thereby getting a faster smelting rate. It will be interesting to note the effect of these high temperatures on the furnace brickwork.

METALLURGICAL CONTROL

Modern copper metallurgy does not consider type slags and mattes; each plant is governed by the ore to be smelted. This is especially true of smelters connected with large single mining units. Ideal conditions for good metallurgical results are a slag containing 37 to 38 per cent SiO_2 ,

39 to 40 per cent FeO , 4 to 6 per cent CaO , and 4 to 6 per cent Al_2O_3 ; matte to be 34 to 36 per cent Cu . Where gold and silver values are high, considerable metal can be saved by judicious use of lime, this factor to be controlled by the economics of individual cases. At plants where excessive silica or alumina is present, the charge has been made less refractory by the use of lime and usually a decided increase in metal-bearing tonnage has been noted.

The proper ratio of base-metal to precious-metal content is of the utmost importance to good metal recoveries. No amount of fluxing can overcome such a deficiency.

When blast furnaces were operated it was found necessary to properly flux all converter slag produced, to avoid high metal losses. When universal reverberatory operation was adopted, it was soon found practical to use the converter slag in a molten condition, thus avoiding the expensive handling and resmelting costs of this by-product. For some time it was thought that metal losses were increased, but when proper fluxing conditions were obtained, it was found that metal losses were actually reduced.

WASTE-HEAT BOILERS

Since increases in fuel consumption have been the key to large tonnages, it has also been necessary to keep waste-heat boiler installation more or less in line. Today we find that waste-heat boiler installations are much more expensive than the furnace proper. In the past, waste-heat boilers were installed in units of 350 to 500 hp., producing steam of 150 to 180 lb. pressure, whereas the latest installations call for boilers of 750 lb. pressure and 1100 hp., equipped with water walls, tracifiers, soot blowers, superheaters and water softeners. Water evaporation at some of the plants is 100,000 lb. per hour per furnace and uses 50 to 55 per cent of the total heat developed.

Converting of copper mattes has undergone very little change in the last 20 years. Two types of converters are now used; namely, Great Falls type and the Peirce-

other factors have considerable bearing on the final outcome; namely,

1. Temperature control by the use of proper grade of silica for the various grades

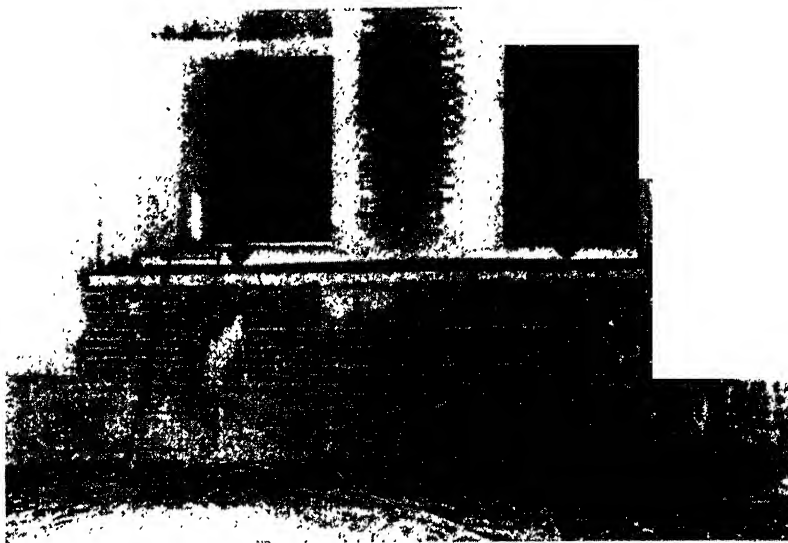


FIG. 4.—STREAMLINED EXIT FLUE AND WATER WALLS, NO. 4 REVERBERATORY FURNACE, HAYDEN PLANT, AMERICAN SMELTING AND REFINING COMPANY.

Smith. During recent years there has been a steady drift to the use of the Peirce-Smith type. The size now commonly used is a 13 by 30-ft. converter. These converters have given the best expression for tonnage and life. Most plants base their tonnage on 37 per cent copper matte at 100 tons per day, increasing or decreasing this figure 5 tons for each per cent of copper above or below 37.

TUYERE LININGS

Considerable variation in life of tuyere lining is being experienced by the various smelters. The length of life varies with the success of the various smelter organizations in putting on magnetite linings; some plants get only 6000 to 8000 tons of copper and others get 50,000 to 60,000 tons per 18-in. repair of the magnesite-brick tuyere lining. While the proper application of the magnetite lining is the controlling factor in the long life of converter campaigns,

of matte.

2. Proper selection of size of each copper charge to be finished.

3. Sufficient expansion left in tuyere brick to prevent excessive spalling.

There have been some improvements in design in recent years of the 13-ft. Peirce-Smith converter. Shells are being butt-welded, making a stronger and smoother job. Trunnion suspension rings and driving gears have been placed on the outside edge of the shell, allowing more space for the tuyeres. The 13-ft. converter now has fifty-two 1½-in. tuyere pipes instead of forty-six. Improved hoods have eliminated the smoke trouble in the converter aisle. Many plants have installed speedier hoisting and faster traveling-crane service. All these changes have made for increased production through smoother operating conditions.

One of the big improvements noted in the use of the Peirce-Smith converter has

been its ability to smelt larger quantities of by-products. This is especially true when the grade of matte is kept below 38 per cent copper. This fact has allowed most converter departments to take care of the major portion of by-products produced.

The problem of dust and fume losses has always been a subject of much concern to copper metallurgists. When true flue dust was the main source of loss, enlarged flue systems and dust chambers were used, but with the increased fineness of the charge and the gradual introduction of low-grade gold, silver and lead siliceous ores as a converter flux, the losses became excessive. To overcome these losses the Cottrell electrical precipitator was installed and has done a wonderful job, saving from 90 to 97 per cent of the metals formerly lost. These installations were first made on converter gases, but today there are installations operating on roaster and reverberatory gases.

During recent years other types of dust-recovery equipment have been used, especially where gold and silver values are low and no great amount of true fume is present. Cyclone separators of the multi-

clone type are being used with very good results, recoveries of 85 to 90 per cent of the true dust being reported.

Smoke and dust control is now a part of every plant. Dustless connections at charging points in both the roaster and copper departments have been satisfactorily worked out at most of the plants. Matte and slag launders are now under suction, allowing little or no smoke to escape. Dust control in the crushing departments has been given much thought and conditions are being improved daily.

AN EVEN BALANCE

A resumé of the changes and improvements made in copper smelting shows a steady and healthy advance. Costs and metal recoveries have been maintained in the face of a steady increase in labor and material costs and an increase in metal content of charge. This has been done by increasing furnace tonnages and conserving metals. Improvements in furnace life and the ability to get better expressions from the fuel burned have also contributed a great deal to keep better than an even balance.

History of Developments in Direct Smelting Practice at the McGill Plant of the Nevada Consolidated Copper Corporation

BY LEONARD LARSON,* MEMBER A.I.M.E.

(Salt Lake City Meeting, September 1940)

BEFORE direct or wet smelting of copper concentrate was adopted at the McGill smelter, in November 1932, actual furnace smelting tests had indicated the possibility of smelting between 400 and 500 dry tons of wet concentrate per furnace day. Under calcine smelting practice, solid charge up to 1165 tons per furnace day had been smelted. It was realized that in order to smelt wet tonnage in equivalent amount per furnace day, a higher combustion rate and higher temperatures would be necessary within the furnace.

The reverberatory furnace considered in the following history of wet-smelting developments is a unit 127 ft. long and 28 ft. 8 in. wide, inside dimensions (Fig. 1). This furnace was in operation through all the years from 1934 to date.

During 1933, the first complete year of direct or wet smelting, the plant was on a curtailed copper-production basis and the available concentrate tonnage to be smelted was limited. The average coal-firing rate in the reverberatory for that year was 124 tons per furnace day. This rate was lower than the average for years immediately preceding under calcine smelting practice. With this coal-firing rate, an average of 391 tons of new metal-bearing material (N.M.B.M.) was smelted per furnace day. The following year, 1934, the coal-firing rate was increased to 139 tons and the smelting rate increased to 448 tons N.M.B.M. per fur-

nace day. In succeeding years production required that either more tonnage be smelted in the one furnace or an additional furnace be placed in operation. With this situation confronting the smelting department, it was determined to continue the program of increasing the coal-firing rate and also to intensify the temperature in the smelting zone of the furnace. In order to accomplish this, various improvements were made to aid combustion within the furnace. The burners were enlarged, increased primary air was supplied to the burners, and changes were made in the furnace to enlarge and streamline the outlet, thus increasing the furnace draft.

The coal-firing rate was increased yearly until 1937 when the firing rate averaged 210 tons per furnace day. Thereafter the firing rate fluctuated according to character of charge and production requirements. In general, however, with the same character of charge the smelting rate increased in almost direct proportion to the increases in firing rate.

Table 1 shows the average coal-firing rate, smelting rate, and other pertinent data for the direct-smelting years of 1933 to 1939 inclusive, the first five months of 1940 and May 1940. These figures show that the water evaporated in the waste-heat boilers was in almost direct proportion to the coal-firing rate. In making comparisons in the table, it should be borne in mind that the figures, except for May 1940, are yearly averages. Because of changes in character of charge or operating conditions, records for individual days or even months

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vary considerably from the yearly average shown, but definite relationships between firing rate and tonnages treated are always evident if fluctuations in the character of charge are taken into account.

With the many increases in firing rate during the period of direct smelting, it is interesting to note that even though there was a considerable variation in the gross fuel ratios, the net fuel ratios were quite uniform (Table 1). This is evidence that the development of greatly increased smelting rates did not adversely affect the fuel efficiency.

With these changes completed, combustion was satisfactory and excessive temperatures in the front of the furnace were reduced. Temperatures were still higher, however, in the front of the furnace than with the lower firing rate for the previous year.

With the higher firing rate the quantity and velocity of gases passing through the furnace increased considerably. This had the effect of increasing the dust burden carried to the flues and boilers by the furnace exit gases. The dust that settled in the flue to the boilers and in the boiler com-

TABLE 1.—*Pertinent Data*

Year	Tons per Furnace Day			Water Evaporated per Furnace Day, Lb.	Furnace Slag		Million B.t.u. per Ton Solid Charge	
	N.M.B.M. Smelted	Solid Charge Smelted	Coal Burned		Cu, Per Cent	SiO ₂ , Per Cent	Gross	Net
1933.....	391	569	124	1,526,000	0.53	36.7		
1934.....	448	637	139	1,635,000	0.61	38.6	6.297	3.027
1935.....	665	701	149	1,471,000	0.41	38.8	5.233	2.834
1936.....	842	901	186	1,816,000	0.39	36.3	4.993	2.648
1937.....	812	906	210	2,126,000	0.39	36.4	5.627	2.806
1938.....	756	790	204	2,039,000	0.41	36.9	6.371	3.285
1939.....	838	903	216	2,355,000	0.39	38.9	5.927	2.831
5 mo. 1940.....	851	900	224	2,614,000	0.34	35.4	6.236	2.824
May 1940.....	854	986	223	2,705,000	0.30	37.2	6.376	2.864

In 1934, with an average firing rate of 139 tons of coal per furnace day, it was found that temperatures at the front of the furnace and in the boilers were excessive. In order to rectify this condition, the furnace draft was raised to the maximum available, but this was not sufficient; it was decided then to enlarge the coal-burner pipes to supply more primary air. In June of 1934 the coal-burner pipes were increased from 6 to 8 in. in diameter and the booster air pipes in these burners were increased from 1 to 1¼-in. diameter. To further improve combustion, a small coal drier was placed in service ahead of the coal-pulverizing mill. With drier coal, finer grinding was achieved in the mill, which in turn speeded up the combustion of the coal. In November the coal-burner pipes were further enlarged to 10 in. in diameter and the booster air pipes were increased to 6 in.

bustion chambers increased materially. Under operating conditions for the previous years, with the lower firing rate and lower velocity of gases, the dust burden was less, but still a large percentage of the dust in the exit gases settled in the flues and boiler combustion chambers. The dust in the combustion chambers was removed periodically but there was a tendency for dust to accumulate in inaccessible places in the flue and boiler entrances. Some of this dust, particularly that near the uptake, smelted and ran back down the front wall into the furnace. The skimming hole was in the front wall of the furnace at this time and the slag skimmed from the furnace was salted to some extent by the smelting of this dust. As shown in Table 1, the copper content of the slag was comparatively high in 1933 but was still higher in 1934. In both years the copper content of the slag reflects

the effect of salting from smelting, which took place in the uptake and the flue. The slag for the year 1934, however, reflects the effect of more salting, caused by increased smelting of flue dust in the uptake and flue due to excessive temperatures incidental to the high firing rate for that year. The metal content of the slag for the year was almost prohibitively high and it was necessary to take steps to correct this condition.

In January 1935 the skimming hole was changed from the front wall of the furnace to the north side. The skimming-hole locations are shown in Fig. 1. With this arrangement the smelted flue dust flowed into the bath at the front of the furnace, where it was exposed to additional smelting and allowed opportunity to settle before being skimmed from the furnace. Lower copper tenor of slags was immediately noted with side skimming practice. The changed position of the skimming hole minimized slag losses but the front wall was still exposed to extreme temperatures, which smelted it away so rapidly that frequent repairs were necessary.

With the skimming hole on the side, it was now possible to alter the construction of the front end of the furnace. The perpendicular front wall of the furnace was removed and a sloping front installed. This accomplished the double purpose of minimizing repairs and streamlining the furnace outlet (Fig. 1). The new front arrangement proved to be a very marked improvement. It was found that upkeep was less, resistance to the gases definitely less, and the metal content of the slag continued to be much lower than before side skimming was initiated.

With a streamlined passage provided for the gases from the furnace, the temperature of the gases entering the boilers was relatively high, and actual smelting of flue-dust settlements took place in the combustion chamber of No. 6 boiler (this boiler being situated directly in front of the furnace outlet, Fig. 1). This increase in tempera-

ture was noted even though the firing rate in the furnace had not been increased.

In view of the extreme heat conditions in the boilers it was determined to equip them with radiant superheaters. This was done in April and May 1935 and July 1936. The boilers were already equipped with convection superheaters therefore each boiler thereafter operated with two superheaters. The installation of radiant superheaters proved entirely successful and waste-heat steam temperatures were raised from 550°F. to about 650°F.

Later in the year 1935, after it had been definitely proved that the sloping front of the furnace was standing up in the face of the high temperatures, the firing rate was further increased and for the last few months of the year it averaged about 160 tons per furnace day. With this rate, even though additional primary air had been provided with a booster fan and better coal grinding achieved by improvements to the coal driers, higher temperatures still were evident in the uptake, flues and boilers. The increased temperatures made it necessary to place siliceous material on the sloping front of the furnace periodically in order to keep it from being smelted away. Experience during the next few months demonstrated that by adding siliceous fluxes as required the furnace front could be maintained indefinitely.

Even though the firing rate in 1935 averaged 149 tons per furnace day compared to 124 and 139 tons respectively in 1933 and 1934 (Table 1), the average waste-heat evaporation rate was lower than for either of these years. Several factors account for this apparent anomaly; namely, changed operating conditions to meet lower production requirements and experimental work in connection with investigation of the use of boilers as economizers. The use of economizer boilers was discontinued in 1935 for two principal reasons: first, because the operation of boilers as economizers was found to be harmful to the tubes

and drums and second, because boilers in series reduced the furnace draft so that the desired combustion and smelting rate could not be maintained.*

In 1936 additional changes were made in the furnace uptake and in the coal-pulverizing equipment. The uptake area was increased in July by removing the relief arch, and in October the furnace outlet was made wider, thus further improving draft conditions. The coal-grinding mill was made longer, additional primary air was provided and a larger coal drier was installed in July and August. These furnace changes, together with coal-pulverizing and burner improvements, made it possible to further increase the firing rate. During a portion of November and all of December two ball mills were operated to furnish coal to the furnace. Thus for those two months the firing rate averaged over 200 tons of coal per day. The December rate jumped to 230 tons per day, and the solid charge smelted for that month averaged 1082 tons per furnace day, the highest smelting rate achieved up to that time with wet smelting. There was a corresponding increase in waste-heat steam generation and the evaporation for the month averaged 2,318,000 lb. per furnace day.

As the firing rate increased during the year more extreme temperatures were noted in the front of the furnace, in the furnace uptake, in the flue and in the boiler combustion chambers. With such extreme temperatures acting on the front slope and on the bottom of the flue to the boilers, both flue dust and brick work were smelted away. In order to relieve this condition holes were cut in the uptake and flue roof and siliceous flux was charged in sufficient amounts to replace whatever smelting took place. Charge holes were also cut in the

furnace roof along the side walls near the front of the furnace. At the end of the year these charge holes extended to within 16 ft. of the skimming hole on the north side of the furnace and to within 11 ft. of the furnace outlet on the south side. Siliceous ores, fluxes or concentrate were charged through these new holes in the roof.

Since the extreme temperatures incidental to the high combustion rate had so changed operating conditions that considerable tonnages were being smelted in the front of the furnace and in the uptake and flue to the boilers, a close check was kept on the metal content of slag skimmed from the furnace. The average copper content of the slag for the year 1936 was 0.39 per cent. During the last five months of the year, all with high firing rate and with increasing amounts of charge smelted in the front portion of the furnace and flues, the copper content of the slags varied from 0.32 to 0.36 per cent. In December, the month that shows the maximum firing and smelting rate, the copper content of the furnace slag was 0.35 per cent. The principal reason for the comparatively low metal content of the slag under smelting conditions as noted above is to be found in the temperature and viscosity of the slag. With the extreme temperatures in the front or skimming portion of the furnace, the temperature of the slag is correspondingly high, and as a consequence is comparatively thin and liquid, thus facilitating the settlement of metal values into the matte.

The analyses of the furnace slags for the year 1936 and December of the same year, together with the matte grades, are shown in Table 2.

TABLE 2.—*Analyses of Furnace Slags*

Period	Analysis, Per Cent					Matte Grade
	Cu	SiO ₂	Fe	CaO	Al ₂ O ₃	Cu, Per Cent
Year 1936.....	0.39	36.3	35.1	6.1	6.0	31.54
Dec. 1936.....	0.35	38.0	35.5	5.1	5.6	30.57

* A paper (by N. W. Sager and H. W. Mossman) covering waste-heat boiler practice at McGill with economizer boilers in service, giving in detail the reverberatory and waste-heat boiler setup at that time, was published in the A.I.M.E. *Transactions* (1933) 106, 237.

With a considerable amount of charge being smelted in the front of the furnace, unsmelted floaters were expected at the skimming hole, but comparatively few were

made wider and an improvement in gas distribution to the boilers was immediately evident. In May the outlet was again made wider and gas distribution to the boilers

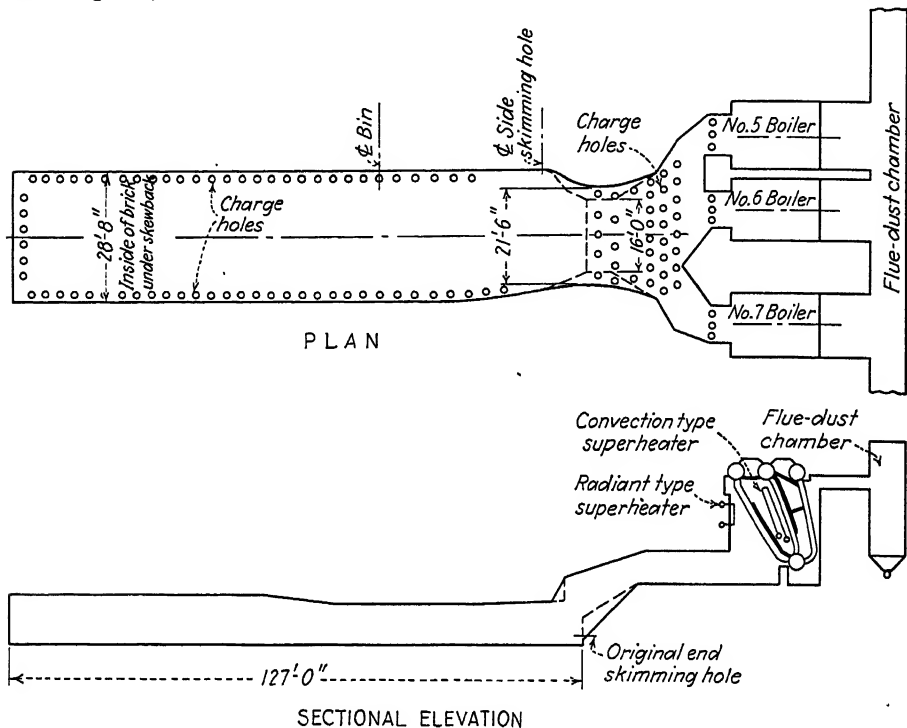


FIG. 1.—INSIDE OF NO. 3 FURNACE, FLUE AND BOILER.

evident. As a matter of fact, floaters were less prevalent under the above smelting conditions than during previous years with low firing rate and with no charge being smelted in the front of the furnace.

Each time that the furnace uptake was enlarged it was found that a better distribution of gases to the waste-heat boilers was achieved. However, with continued high smelting and firing rates in effect, it was desirable to provide a still more even distribution of waste gases to the boilers. Efforts were made to equalize the gas distribution by means of the rear boiler dampers, and some success was achieved by manipulating these dampers, but it was impossible to get the distribution desired. In February 1937, the furnace outlet was

again improved. With the wider outlet it was now found possible to operate the furnace at about three-fourths of maximum smelting rate with only two of the three boilers in service. Previously with one boiler out of service it was necessary to cut the firing rate severely.

Fig. 1 shows a plan and elevation of No. 3 furnace and the waste-heat boilers. The broken lines indicate the shape and size of the furnace outlet and uptake before the changes noted in this paper were made. The sketch also shows the original and changed location of the skimming hole, and the present location of charge holes in the arch of the furnace, uptake and flue. There has been no further enlargement of the furnace outlet and the furnace and

boilers have operated with the outlet about as shown until the present time.

During the years 1937, 1938, 1939, and 1940 to date, the rates of firing, smelting, and waste-heat steam generation were fairly high (Table 1). In general the firing rate was determined by the smelting rate required. During this period operating conditions enabled the power plant at all times to utilize profitably the waste-heat steam produced. If the tonnage of concentrate to be smelted during a certain period was limited, additional custom ores and fluxes were added to the charge so that

higher combustion and waste-heat steam-generation rates than any like periods since direct smelting was initiated. A relatively high copper-production rate was desired during these periods and as a consequence the furnace charge at the smelting end of the furnace consisted almost entirely of concentrate and basic fluxes. On the front slope of the uptake and in the flue to the boilers over 20 tons of siliceous and semi-siliceous fluxes was smelted per furnace day in order to protect the refractories on the floor of the uptake and flue. Also, a monthly average of from 28 to 75 tons of

TABLE 3.—*Tonnage Smelted*
Dry Tons per Furnace Day

Concentrate	Custom Ore and Flux	N.M.B.M.	Limerock	Secondaries	Total Solid Charge
822	32	854	17	25	896

Average moisture content, 9.22 per cent H_2O .

both the smelting rate and steam-generation rate could be maintained.

During various periods it was necessary to operate the furnace with a relatively high proportion of siliceous or semi-siliceous fluxes in the charge. The most refractory charge smelted over a period of a month was that smelted during the month of May 1939. During that month 873 tons of solid charge containing 166 tons of siliceous flux were smelted per furnace day. The fuel-combustion rate for the month was 227 tons per furnace day and waste-heat steam generated was 2,514,000 lb. per furnace day. The net fuel ratio was 2.979 million B.t.u. per ton solid charge. The slag produced contained 0.42 per cent Cu, 44.1 per cent SiO_2 , 37.3 per cent Fe, 5.9 per cent CaO, and 7.0 per cent Al_2O_3 . The furnace performance under these conditions indicates that it is quite possible to smelt refractory charges with direct smelting and still achieve good furnace efficiencies.

The year 1940 (January to May, inclusive) and the month of May 1940 show

concentrate per furnace day was charged through the holes in the furnace roof at the front end of the furnace during these periods. It is interesting to note the relatively low copper content of the furnace slags under these smelting conditions. Experience during the periods named indicates that relatively clean furnace slags are possible even though the front end, uptake and flues of the furnace are doing a portion of the smelting.

TABLE 4.—*Waste-heat Steam*

Net Pounds Water Evaporated per Furnace Day	Average Temperature and Pressure at Waste-heat Boilers		
	Feed Water, Deg. F.	Waste-heat Steam, Deg. F.	Gauge Pressure, Lb. per Sq. In.
2,709,000	200	624	212

Tables 3 to 6, inclusive, show the tons of various characters of material smelted during May 1940 with British thermal units in connection with coal burned, steam generation, etc., also the analyses of the

new metal-bearing material smelted and slag produced.

Tonnages considerably in excess of those for May 1940 have been smelted but when operating at these higher smelting rates the furnace charge was less refractory and the slags produced were lower in silica. If increased smelting rates should be de-

to accelerate the combustion rate of pulverized coal. If all or part of the primary air were preheated, temperatures in the smelting zone could be increased perhaps 100° or 200° Fahrenheit. With higher temperatures in the smelting zone the smelting rate would be materially increased. The extreme temperatures, however, would be

TABLE 5.—*B.t.u. Data*

B.t.u. per Pound		Million B.t.u. per Furnace Day		Percentage of Recovery
Coal	Steam	In Coal	In Steam	
12,810	1,164	5,714.9	3,148.5	55.1

B.T.U. RATIOS

Per Ton Solid Charge			Per Ton N.M.B.M.		
Million B.t.u. Gross from Coal	Million B.t.u. Recovered in Steam	Million B.t.u. Net Chargeable to Furnace	Million B.t.u. Gross from Coal	Million B.t.u. Recovered in Steam	Million B.t.u. Net Chargeable to Furnace
6.376	3.512	2.864	6.692	3.687	3.005

TABLE 6.—*Tonnage, Grade and Analyses*
REVERBERATORY N.M.B.M. TREATED

Dry Tons	Analysis								Slag Analysis, Per Cent					Matte Grade
	Oz. per Ton		Per Cent											
	Au	Ag	Cu	SiO ₂	Fe	CaO	Al ₂ O ₃	S	Cu	SiO ₂	Fe	CaO	Al ₂ O ₃	Cu, Per Cent
20,069	0.207	0.880	24.04	5.6	30.0	0.5	2.0	34.6	0.30	38.0	35.7	3.8	6.8	29.73

sired with the character of charge smelted in May it is doubtful whether this could be achieved with the present size of furnace and the waste-heat boiler setup. Further increases in the tons of coal fired would involve excessive velocities in the furnace, flues and boilers; higher draft would be required and it is doubtful whether the boilers could be kept open with the extra burden of dust and additional temperatures involved. The answer to the problem of further increasing smelting rates may be found in the use of preheated primary air

severe on the furnace arch but experience only could determine how long the arch would last under these conditions.

High temperature is particularly desirable for wet smelting because the initial slags produced are relatively high in silica and alumina and therefore are very refractory. The highly siliceous slag left on the face of the charge (with side charge practice) after the matte has run off into the bath, is stiff and viscous at ordinary smelting temperatures and runs off into the slag bath at a comparatively slow rate. If

temperatures are raised the slag becomes more fluid and runs off rapidly, thus exposing fresh charge to the action of the flame. With the rapid removal of slag film from the face of the charge, leaving a fresh surface exposed, a material increase in the rate of smelting can be achieved.

DISCUSSION

C. R. HAYWARD.*—This interesting paper, particularly as regards changes to increase capacity, brings back recollections of similar efforts made about 25 years ago, stimulated by increasing demands for copper due to the first

World War. One of the most noteworthy developments in furnace design at that time was made by Colonel H. H. Stout at the Copper Queen plant, where, by a considerable enlargement of the gas exits from the furnace, he was able to burn more fuel and thereby smelt more charge. This, together with changes in furnace lines or firing methods at other plants, greatly stepped up copper production without enlargement of the furnaces. In fact, at about this time shorter furnaces began to be common.

Mr. Larson is discussing the smelting of raw charge, which introduces new factors in smelting practice, but it is fair to assume, because of past history, that the improvements in smelting rate that he mentions will suggest further economies in direct smelting of raw concentrates stimulated by present market conditions.

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New Reverberatory Waste-heat Boiler and Power Plant at Douglas Smelter

By L. L. McDaniel,* Member A.I.M.E.

(Tucson Meeting, November, 1938; New York Meeting, February, 1939)

DURING the past few years a number of improvements in smelting and power equipment have been made at the Douglas smelter of the

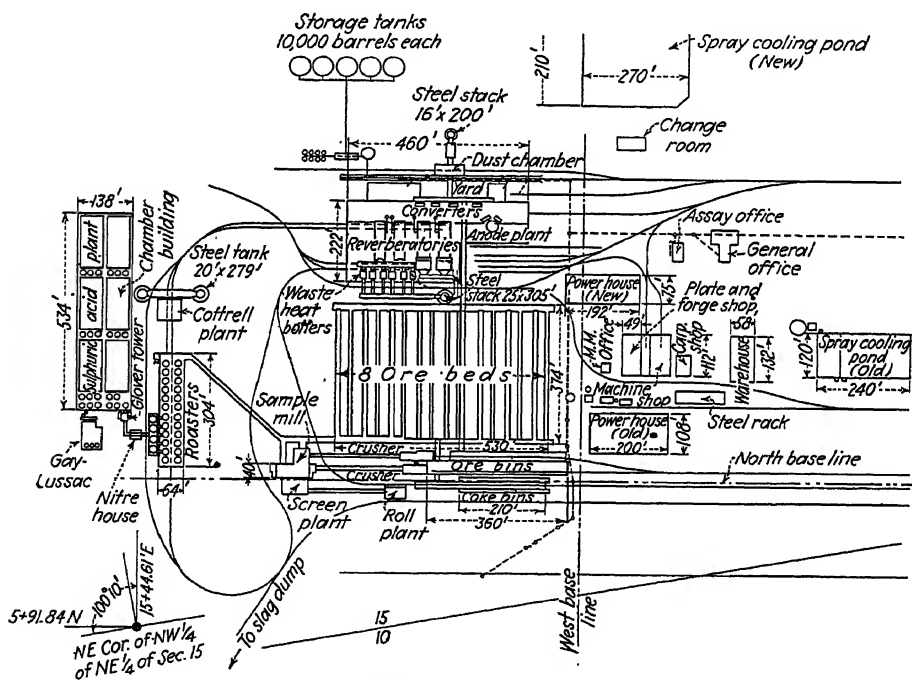


FIG. 1.—GENERAL PLAN OF SMELTER.

Phelps Dodge Corporation at Douglas, Ariz. In the summer of 1935 work was started on the first unit of a new reverberatory waste-heat boiler plant which ultimately was to furnish steam for a modern high-pressure power plant. A second reverberatory waste-heat boiler unit

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* Phelps Dodge Corporation, Douglas, Arizona.

was completed in 1937 and the new high-pressure power plant was placed in operation early in 1938. These changes relate primarily to improvements in waste-heat steam recovery and in electric power generation.

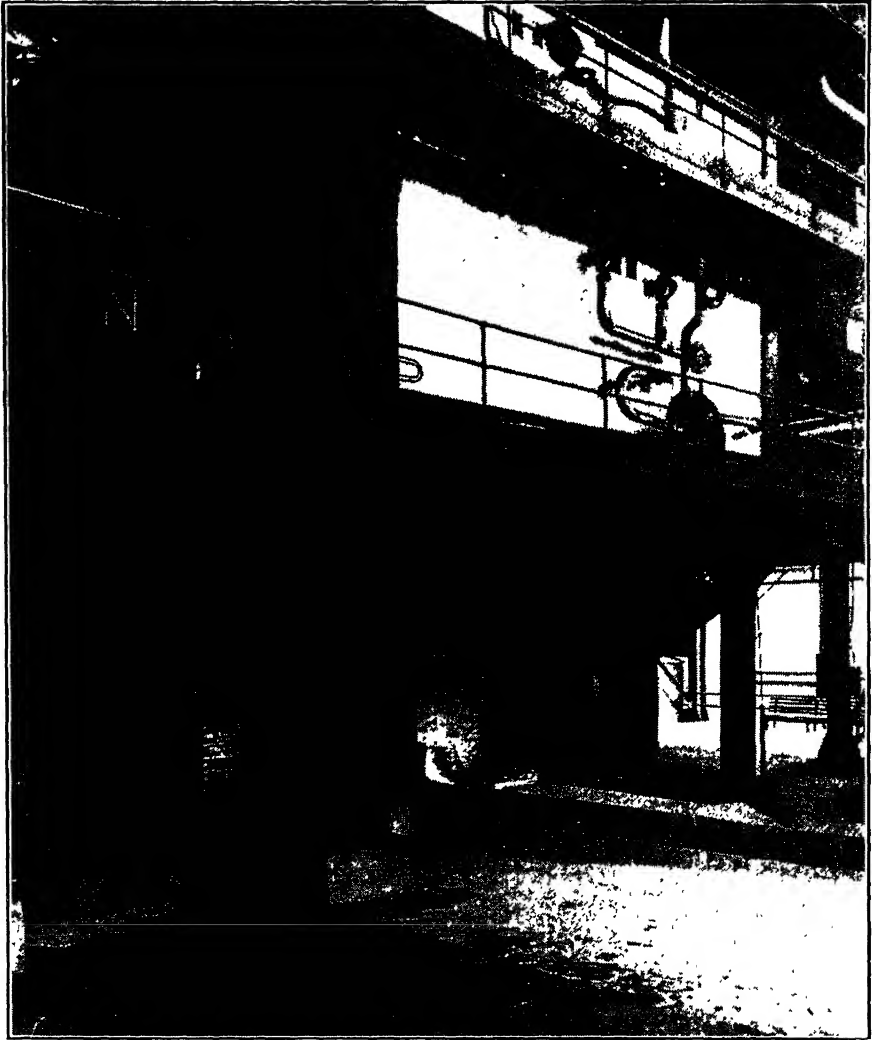


FIG. 2.—SKIMMING END OF No. 7 REVERBERATORY, SHOWING SUPERIMPOSED WASTE-HEAT BOILER.

All surplus electrical power at Douglas is used in the Copper Queen mines at Bisbee, 25 miles away, and waste-heat power at Douglas is therefore an important item. A general plan of the smelter is shown in Fig. 1.

The outstanding feature of design in the new reverberatory-boiler units is the location of the boiler directly over the skimming end of the furnace (Fig. 2), with the boiler tubes exposed to the molten bath in the

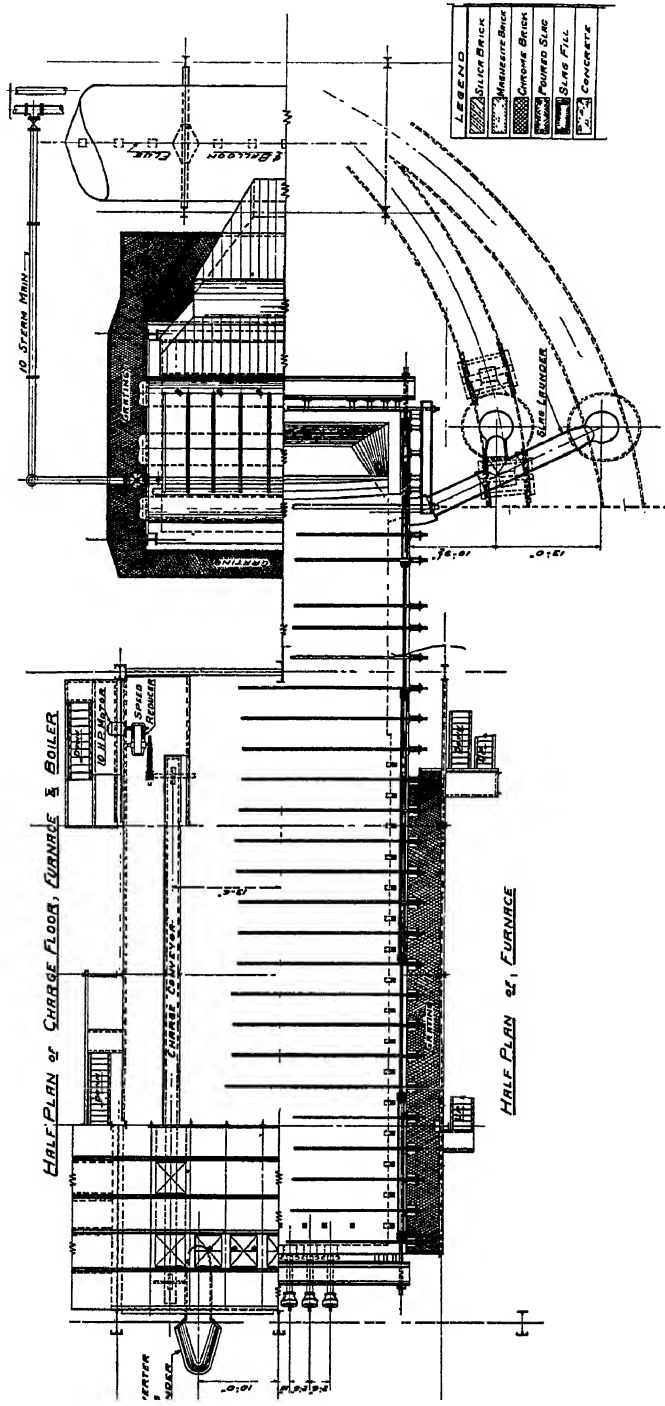


FIG. 3.—PLAN AND CROSS SECTION OF NO. 7 REVERBERATORY FURNACE AND BOILER.

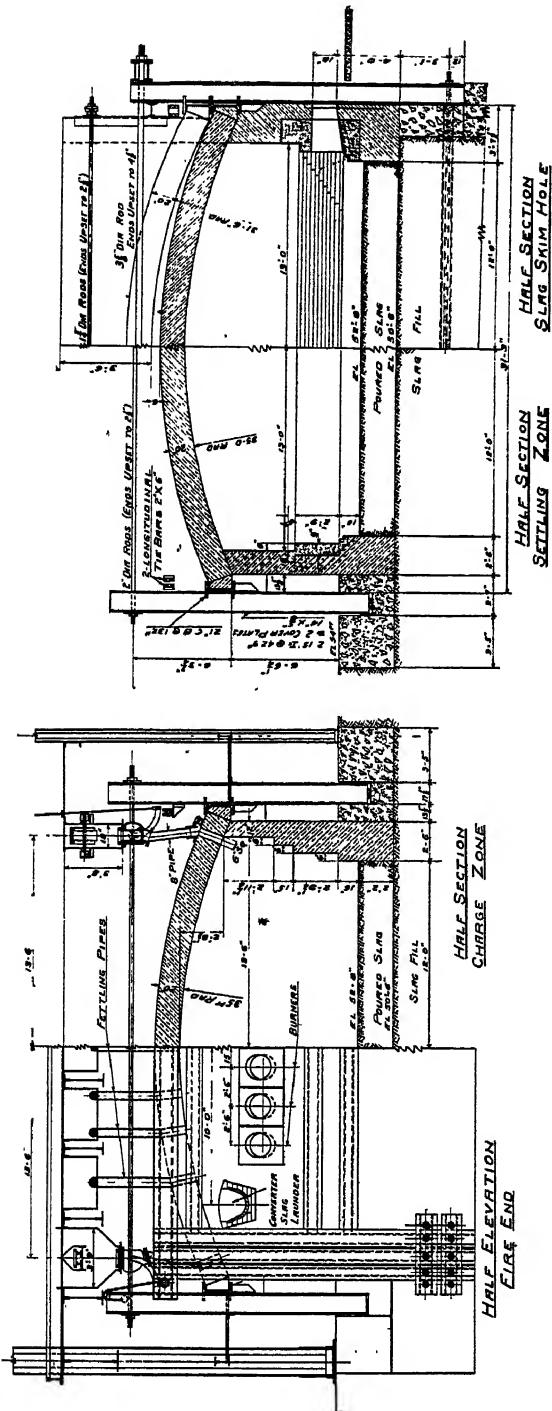


FIG. 3.—(CONTINUED.)

furnace and with no damper between the furnace and the boiler. During more than two years of continuous operation there has been no reason for altering or modifying this arrangement in any way. Waste-heat recovery has been greater than was ever attained with the conventional design of

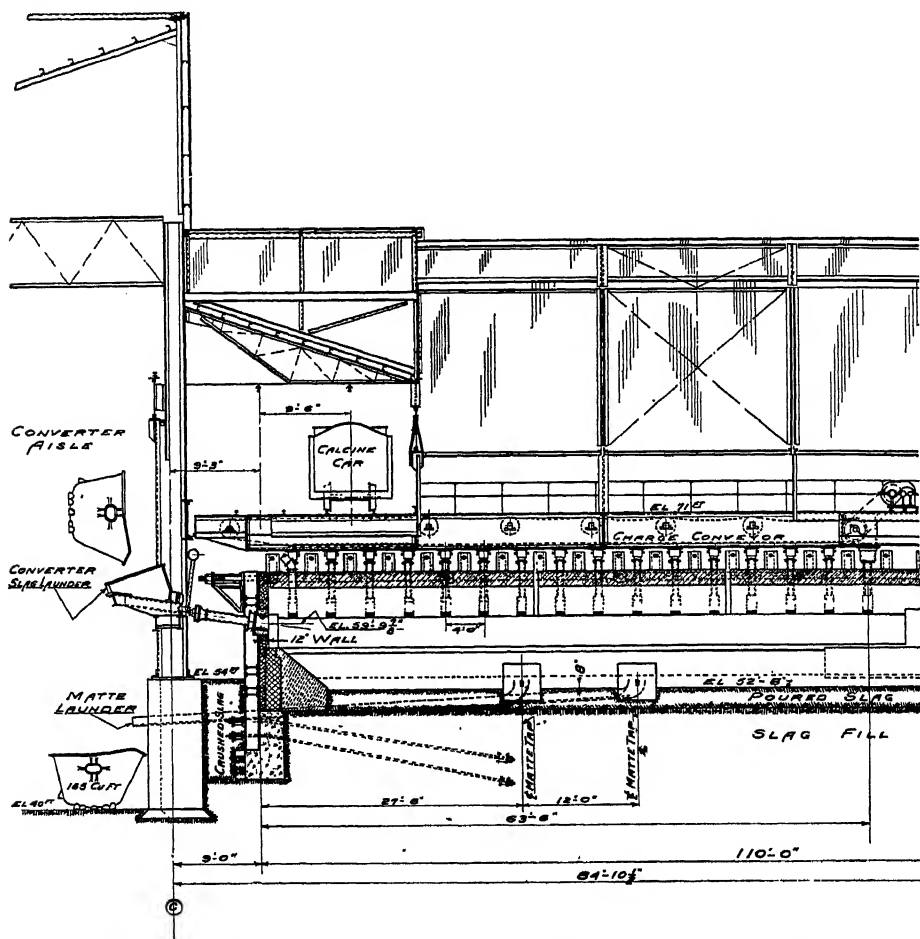


FIG. 4.—LONGITUDINAL SECTION OF NO. 7 REVERBERATORY AND BOILER.

furnace and boilers separated by flues, while economy of furnace operation has been improved through elimination of brick expense on these flues.

REVERBERATORY FURNACES

The reverberatory furnaces are 107 ft. long and 26 ft. wide, inside measurements. The arch is horizontal for its full length, without droop or restriction at the outlet. The full opening of the outlet area exists for only a short time after the furnace is put into operation, because the dust removed from the boiler tubes by hand lancing falls into this area

and gradually reduces the size of the opening, the furnace temperature at this point being too low to smelt the dust completely. This filling up of the outlet of the furnace, however, has presented no serious problem to operations. - The first furnace, No. 7, was run for a year and a half before shutting down to remove this material and it is probable that a

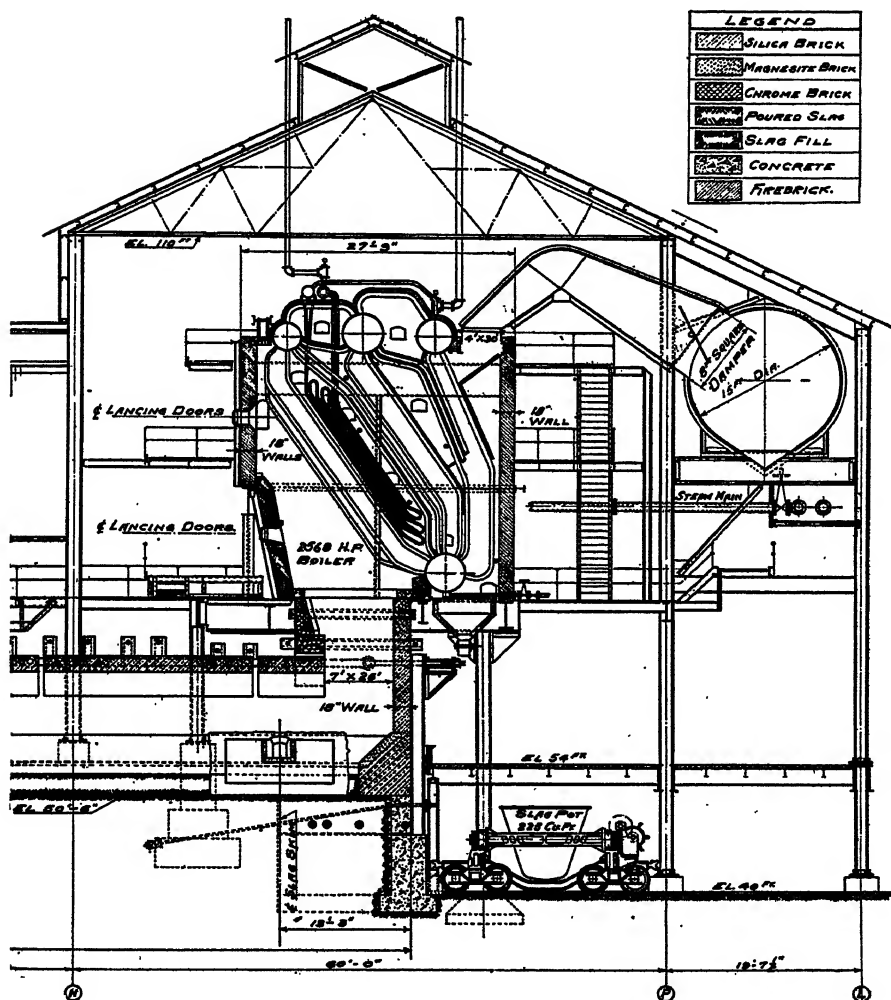


FIG. 4.—(CONTINUED.)

method could be worked out for doing this while the furnace is in operation if desired. (Figs. 3 and 4.)

Silica brick is used in the arch and walls of the furnaces, with magnesite brick in the bridge wall and in protective panels in the side walls at the end of the charging zone. With the spray-gun patching method of

renewing silica brick arches as developed at the United Verde Branch, Phelps Dodge Corporation, which is now being used at Douglas, furnace campaigns probably can be lengthened to about one year, which fits in well with a desirable operating period for the boiler and for cleaning out the furnace bottom and outlet area.

Following practice at El Paso and elsewhere, the bottoms of these furnaces were poured in place with liquid slag, the slag being drawn from an adjoining operating furnace. About 6 ft. of liquid slag was first poured as a fill. Anchor bolts for the end steel bindings were embedded in this poured slag. The final 24 in. of slag, constituting the actual furnace bottom, was poured after the furnace walls were laid. In both No. 7 and No. 8 furnaces a false bottom of magnetite several feet thick was removed after a year or more of operation, and at that time the poured slag bottoms were found practically unaltered at their original elevation, with no appreciable penetration of matte.

Smelting mixture for the reverberatory furnaces is composed of ore and concentrate. The hot roasted charge is delivered to the furnaces in 30-ton larry cars and is fed by drag chain conveyors into 8-in. charge pipes spaced at 4-ft. centers. The charging zone extends 60 ft. from the bridge wall. This method of charging has been used successfully for many years. The furnaces average 1000 tons solid charge per day with a fuel ratio of 3.00 million B.t.u. per ton. The furnaces are fired with natural gas, which is burned in six high-pressure burners on each furnace. Water-jacketed burner tunnels formerly were used but have been replaced by refractory tunnels made of magnesite brick or cast of magnesite ganister. Gas pressure at the burners at present is 15 lb., the pressure being closely controlled by very sensitive pressure regulators. The present volume of gas burned is 120,000 cu. ft. per hour, containing 1060 B.t.u. per cubic foot. Combustion gases, sampled 70 ft. from the burners, contain 0.6 per cent oxygen. The arch temperatures in the combustion zone average about 2500° F., with a drop to 2300° F. at the exit end of the furnace. Furnace draft is 0.02 in. of water at a point 20 ft. from the exit end.

Matte is tapped through the side of the furnace, the two tap holes being 27 ft. 6 in. and 39 ft. 6 in., respectively, from the bridge wall. Tapping plates are cast from anode copper, using a magnesite brick core. Matte launders are cast from anode copper in rather heavy sections. Slag is skimmed through the side of the furnace 11 ft. 6 in. from the front wall at the boiler end of the furnace. Tracks are arranged to allow two pots to be skimmed without shutting off the slag stream. Side skimming is a necessity in these furnaces because of the chilling effect of the boiler directly over the slag bath, and also to avoid fouling from the high-grade sintered dust dislodged from the boiler tubes during hand lancing. No trouble from chilled bath or fouled slag has been found in the present side-

skim location. Cast-steel launders are used for skimming furnace slag and also for receiving converter slag, which is poured through the bridge wall on one side of the burners. Buckstays, tie rods and end steel bindings are as shown in the drawings.

WASTE-HEAT BOILERS

The single waste-heat boiler on each furnace has 25,680 sq. ft. of heating surface and is now operating at 75 per cent of rating and producing 60,000 lb. of steam per hour. The boilers were designed for 400 lb. pressure and 644° F. steam temperature, but at the time they were installed the steam-plant requirements were for steam of 165 lb. pressure and 460° F. temperature. These requirements were met by leaving out two-thirds of the pendant superheater tubes. When the new high-pressure power plant was completed early this year, the boilers were converted to high pressure by installing the remaining superheater tubes. In order to allow more space for these additional tubes, one row of boiler tubes was removed from No. 7 boiler, the tube holes being closed with welded plugs. No. 8 boiler was designed without this row of tubes. The conversion of the boilers required the shutting down of each furnace for about one month.

Firebrick was used in the boiler walls. On No. 7 furnace, the sloping wall between the furnace arch and the boiler wall was laid with silica brick, while on No. 8 boiler a suspended wall with firebrick shapes was used. Both walls have given satisfactory service. The boiler front wall has two tiers of 10 doors each for hand lancing with air at 80-lb. pressure. In addition, No. 8 boiler has a row of six telescopic soot blowers across the front of the boiler above the hand-lancing doors. These blowers use superheated steam and are very effective in removing the loose dust near the top of the tubes, where the heat has not been sufficient to cause sintering. Both boilers are equipped with soot blowers on all banks of tubes, using superheated steam. Dust from the boilers is removed once a week from the small hoppers back of the mud drum and from the balloon flue leading to the 300-ft. reverberatory stack. The amount of dust passing through the boiler at the low gas velocity is very small, a week's accumulation amounting to about 8000 lb. for each boiler.

Feed-water pumps are in the new power house, 500 ft. from the boilers. The operating pump is an electrically driven three-stage centrifugal pump with a capacity of 175,000 lb. of feed water per hour. There are also two steam-driven stand-by feed-water pumps in the power house, and one at the boilers with fresh-water connections for emergency use. Feed water is deaerated and heated in the power house, then pumped to the boilers through duplicate 6-in. insulated lines with automatic control at the pumps and boilers. The temperature of feed water

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at the boilers averages 275° F. A single 12-in. insulated line conveys the steam from the boilers to the powerhouse. Evaporators in the powerhouse supply distilled water for feed-water make-up, which amounts to about 5 per cent.

Complete data on boiler operations are recorded by meters grouped on a panel near the boilers. This information, together with a few additional observations, gives a complete record of boiler performance, from which boiler efficiency is readily calculated. The efficiency over a two-year period has shown a consistent unaccounted for gain of about 7 per cent, which is attributed to radiant heat from the incandescent slag bath to which the boiler tubes are exposed. A monthly operating record of furnace and boiler is shown in Table 1.

TABLE 1.—*Operating Data for June, 1938*

	Reverberatory No. 7	Reverberatory No. 8	Average
Furnaces:			
Tons charge per day.....	1,029	1,004	1,016
Gas burned, million B.t.u. per day.....	3,030	3,029	3,030
Fuel ratio, million B.t.u. per ton.....	2.94	3.02	2.98
Boilers:			
Feed water, lb. per hour.....	60,390	61,340	60,865
Blow down: soot blowers, etc.....	911	1,977	1,444
Steam produced, lb. per hour.....	59,479	59,363	59,421
Feed-water temperature, deg. F.....	274	274	274
Steam temperature, deg. F.....	637	689	663
Steam pressure, lb. gauge.....	346	346	346
Boiler-hp. developed.....	1,933	1,978	1,955
Percentage of boiler rating.....	75.32	77.02	76.17
Actual evaporation, lb. per 1000 B.t.u.....	0.471	0.470	0.471
Equivalent evaporation, lb. per 1000 B.t.u.....	0.528	0.541	0.535
Temperature gases to boiler, deg. F.....	2,220	2,279	2,250
Temperature gases from boiler, deg. F.....	516	516	516
Percentage of fuel to steam.....	51.25	52.51	51.88
Boiler heat balance:			
Heat in gases to boiler, million B.t.u. per hour.....	74.6	76.9	75.7
Heat in gases from boiler, million B.t.u. per hour....	16.8	16.7	16.7
Heat available for steam, million B.t.u. per hour....	57.8	60.2	59.0
Heat transferred to steam, million B.t.u. per hour....	64.7	66.2	65.4
Heat unaccounted for, million B.t.u. gain.....	6.9	6.0	6.4
Heat unaccounted for, per cent gain.....	9.2	7.8	8.5

POWER PLANT

The floor plans and end sections of the new powerhouse are shown in Figs. 5 to 8. The operating floor is 15 ft. above ground level, with the basement at ground level. Main equipment is on the

operating floor. Equipment installed at the present time is based on operation of two high-pressure waste-heat boilers, with space allowed for additional equipment as required. Equipment for generating alternating current consists of two turbo-generator sets with 5000-kw., 2300-volt, three-phase, 60-cycle generators direct-connected to 15-stage, 3600-r.p.m. turbines operating at 340-lb. gauge steam pressure and 660° F. temperature. Steam is extracted from the turbines at two points for feed-water heating. The generators have direct-connected exciters

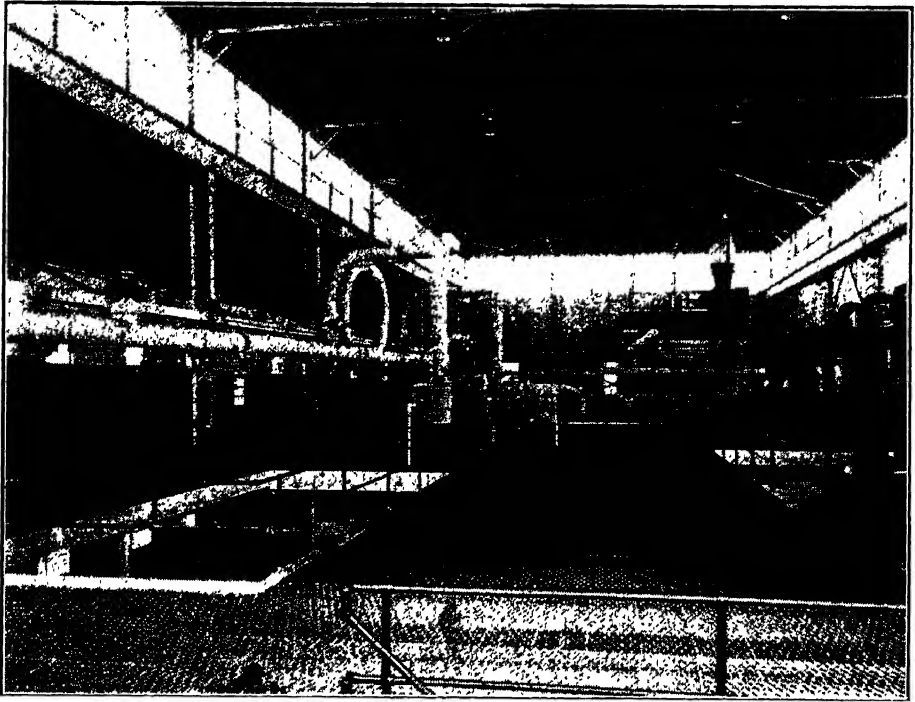


FIG. 5.—OPERATING FLOOR, NEW POWER HOUSE.

and the generator coils are cooled by surface air coolers using condenser water. Each turbine is connected to a surface condenser with air ejector and duplicate condensate pumps. Condenser cooling water is circulated by centrifugal pumps of 5700 gal per min. each, one pump being provided for each condenser with a third pump in reserve. Condenser outlet water is pumped through wood-stave pipes to a spray cooling pond in which the water is kept free from algae by chlorine gas.

Steam consumption of the turbines at full load averages 11.65 lb. of steam per kilowatt-hour with a vacuum (absolute pressure) of 1.25 in. Hg. This is equivalent to 13,000 B.t.u. per kilowatt-hour based on total heat transferred to steam. Each turbine, operating at full load, takes the total steam produced by one reverberatory waste-heat boiler. Occasionally,

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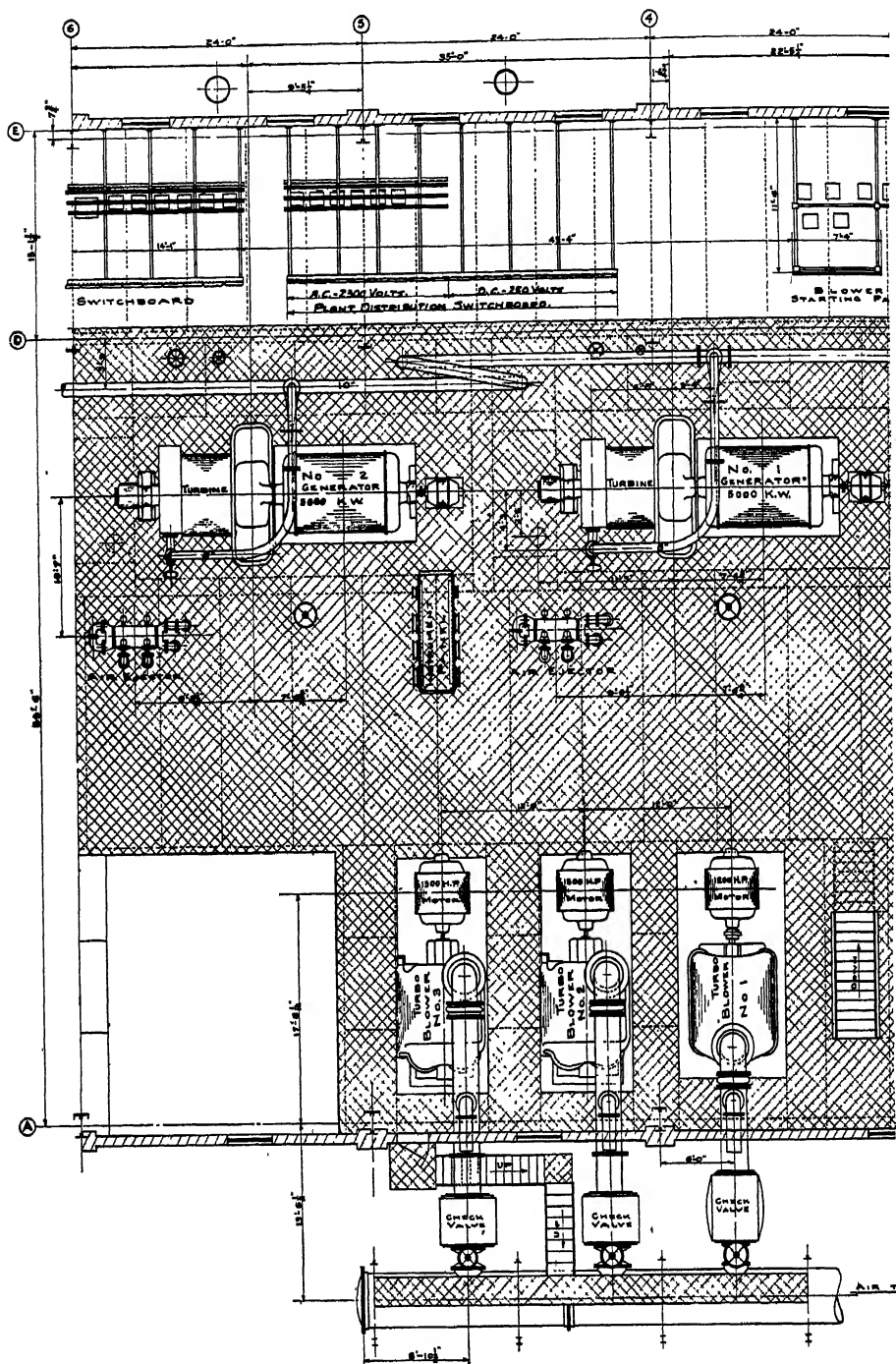


FIG. 6.—PLAN OF OPERATING FLOOR, HIGH-PRESSURE POWER PLANT.

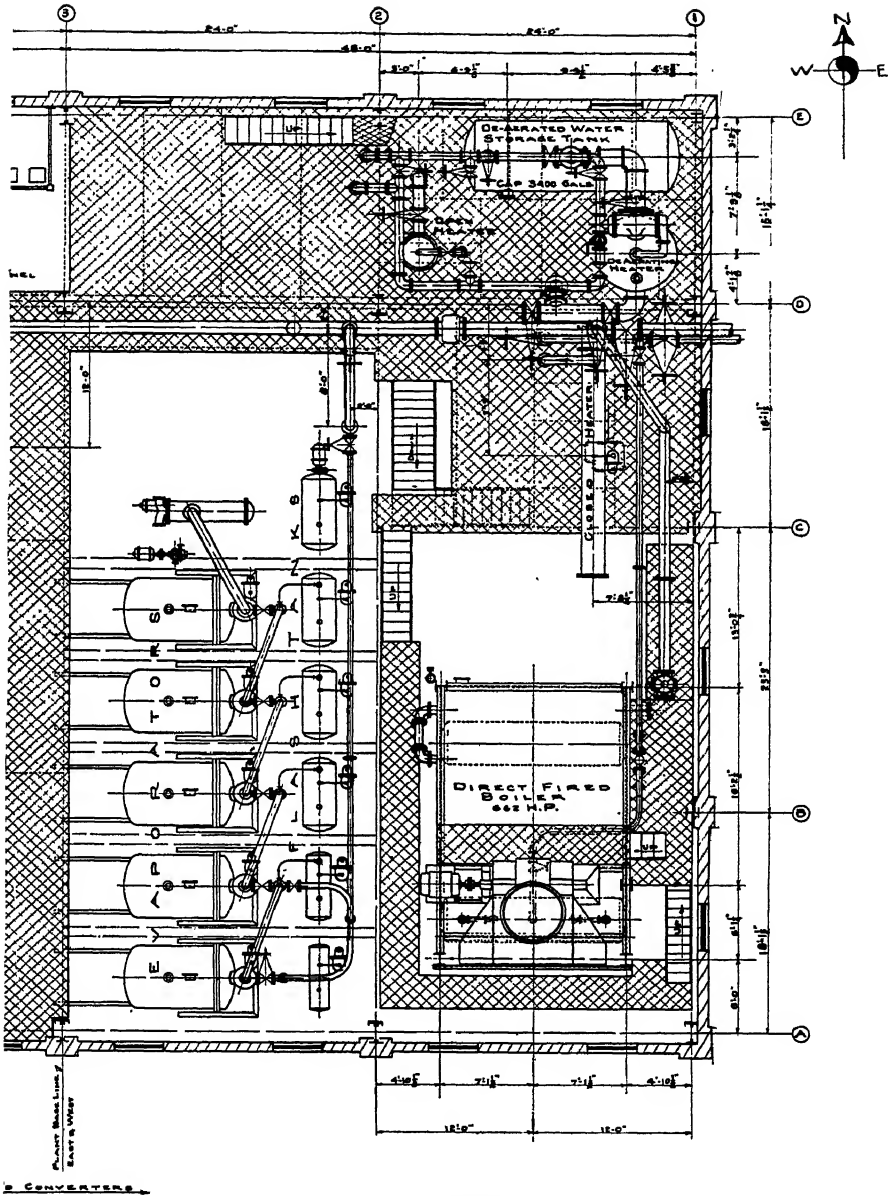


FIG. 6.—(CONTINUED.)

during periods of light electric load, it is necessary to impair the vacuum at the turbines in order to increase the steam consumption, thus avoiding blowing off steam at the boiler with a corresponding waste of distilled water. The vacuum is impaired by admitting air to the condensers.

In case of interruptions to the waste-heat boilers there is a stand-by direct-fired boiler in the power house ready to pick up the load. This is a

662-hp. water-wall boiler, operating at 300 per cent of rating. The boiler is fired with natural gas through five burners. Combustion air is induced by a fan mounted on top of the boiler and discharging the exit gases into the stack. Combustion control is entirely automatic. Burners and air shutters are controlled by steam pressure, the boiler responding instantly to variations in demand for steam. Efficiency of the direct-fired boiler at full load averages 76.0 per cent.

A deaerating feed-water heater uses steam extracted from the turbines at 2-lb. gauge pressure to heat the feed water to boiling, to eliminate oxygen. The deaerated feed water is then heated to 280° F. in a closed heater in the discharge line of the feed-water pumps, using steam extracted from the turbines at 60-lb. gauge pressure for this purpose. There is also an open feed-water heater, which is used only in emergencies or when starting up. Distilled water for boiler feed-water make-up is produced in a multiple-effect evaporator operated with high-pressure steam. The evaporator operates in five stages, any one of which may be taken out of service without interrupting the production of distilled water. The evaporator operates continuously at a present rate of 5800 lb. of distilled water per hour with distilled water produced equaling 4.41 lb. for each pound of steam used. A power-house operating record is shown in Table 2.

TABLE 2.—*Power Data, June, 1938*

	Set No. 1	Set No. 2	Average or Total
Steam to turbine, lb. per hour.....	58,234	59,766	59,000
Steam pressure, lb. gauge.....	340	340	340
Steam temperature, deg. F.....	660	660	660
Condenser inlet temperature, deg. F.....	83	83	83
Condenser outlet temperature, deg. F.....	100	102	101
Vacuum,* in. Hg (abs. pressure).....	2.90	2.70	2.80
Power factor, generators.....	0.93	0.92	0.93
Kilowatt-hours generated, avg.....	4,846	4,804	4,825
Steam per kilowatt-hour, lb.....	12.02	12.44	12.23
Steam to evaporators, lb. per hour.....			1,315
Steam from waste-heat boilers, lb. per hour.....			118,842
Steam from direct-fired boilers, lb. per hour.....			975
Total steam, lb. per hour.....			119,817
Steam used, lb. per hour.....			119,315
Steam unaccounted for, lb. per hour.....			502
Steam unaccounted for, per cent.....			0.42

* Includes impaired vacuum.

Converter air, at 14 lb. pressure, is supplied by three electrically driven turboblowers, each delivering 20,000 cu. ft. per min. Each blower is equipped with a power wheel or impedance vanes to control the air volume and to reduce the power loss when operating at less than

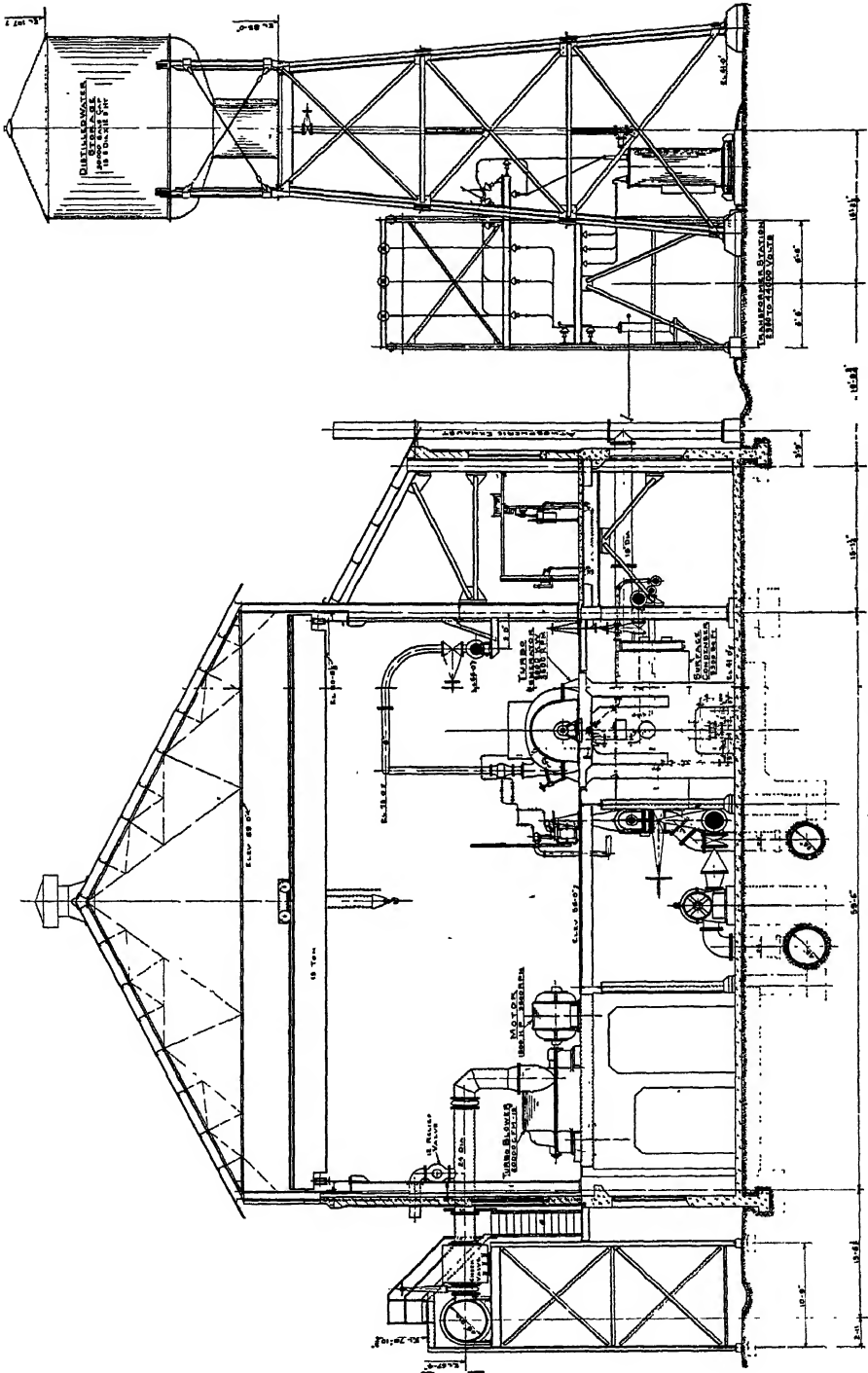


Fig. 7.—TYPICAL CROSS SECTION, NEW POWER PLANT.

full capacity. The blowers operate at constant pressure, with automatic regulators controlling the power wheels. The three blowers discharge air into a 48-in. converter air main. Total air volume delivered through the main is measured by an orifice meter in the powerhouse, while air

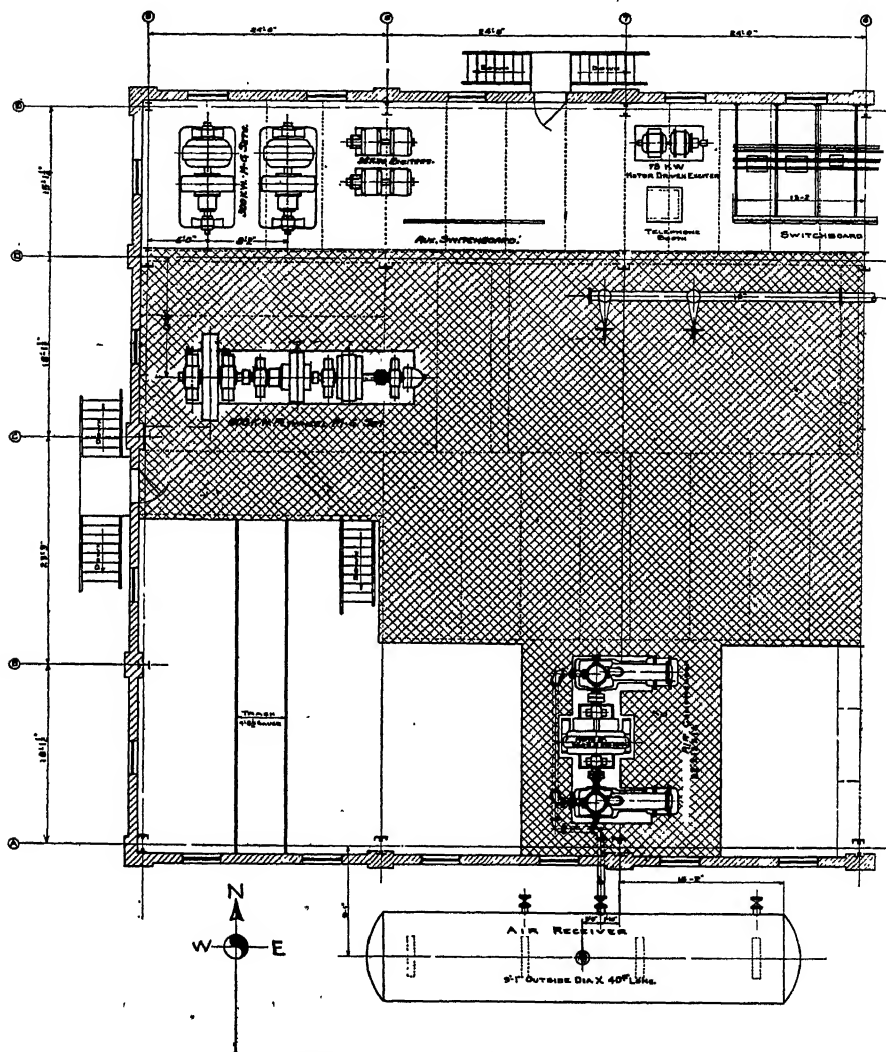


FIG. 8.—BASEMENT FLOOR PLAN, COLUMNS 6 TO 9.

consumption at the converters is measured by indicating and recording meters at each of the four converters. Air production averages 1165 cu. ft. of air, at 12.8 lb. barometer and 100° F. temperature, per kilowatt-hour. Automatic control of the blowers and general blower performance has been entirely satisfactory. Soundproofing around the air intakes

and the use of mufflers on the atmospheric exhaust pipes have materially lessened the noise from the blowers.

Direct current to operate converters, cranes and electric locomotives is generated by a 600-kw. flywheel motor-generator set, with two 300-kw. motor-generator sets as reserve equipment. If both the direct current generator and the turboblowers were put out of service by a power failure, the flywheel could furnish sufficient power to turn down the four converters and to allow the cranes to be moved. An automatic turn-down system for the converters under these conditions is being given consideration. High-pressure air is produced by a 2700-cu. ft. per min. compressor. Compressed air at 90 lb. pressure is delivered to a receiver outside of the powerhouse and from there is distributed to plant service lines. Switchboard panels for operating powerhouse equipment and for distribution lines are at the level of the operating floor. Recording and indicating meters are used on each circuit, all circuits being protected by overload circuit breakers and external lightning arresters. Plant distribution is made through transformers, to reduce the voltage from 2300 to 440 volts. Current for transmission to the Copper Queen mines at Bisbee passes from the switchboard through two separate lines to transformers in a substation outside of the building, where the voltage is stepped up from 2300 to 44,000 volts. The transformer station is composed of six 2000-kva. transformers, oil-insulated, self-cooled and sealed with nitrogen gas. Three high-tension transmission circuits are available between Douglas and Bisbee. Two circuits are in regular use and the third is held in reserve as an emergency circuit during storm periods. Transformer and line losses amount to about 5 per cent.

Performance of the new furnaces, boilers and power plant has been entirely satisfactory, most of the estimated economies being exceeded by operating results.

DISCUSSION

P. T. BENSON.*—Have there been any tube failures with the boiler described? If so, how was the repair accomplished? If not, what are the plans for taking care of possible tube failure?

P. D. I. HONEYMAN.†—As Mr. McDaniel could not attend the meeting, I presented his paper, therefore he has asked me to write my answer to the question regarding tube failures

in the waste-heat boiler described in his paper. As I recall, my answer was to the effect that so far there have been no tube failures in the boiler. At the end of each furnace campaign the boiler undergoes rigid inspection, and any weak or suspicious tubes are removed. In the event of tube failure while operating, fuel would be immediately cut off the furnace and all doors to the setting would be opened. As soon as possible a corrugated iron bulkhead would be inserted across the furnace through the expansion joint in the arch close to the boiler. Boiler-feed pumps would be kept operating until the boiler had been cooled down, when the tube would be replaced.

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Clarkdale Method of Hot-patching Operating Furnaces

By C. R. KUZELL,* MEMBER A.I.M.E.

(Tucson Meeting, November, 1938; New York Meeting, February, 1939)

ALTHOUGH furnaces constructed of refractory brick have been operated for many decades, there has always been an unfulfilled desire by the operators for a less arduous and more satisfactory method of patching weak spots and burned-out zones in order to postpone and to effectively extend the termination of a furnace campaign. Not only has this desire frequently arisen when small spots have approached incipient failure while the furnace structure as a whole was still in good condition, but also when larger areas showed signs of needing replacement. The available methods have been arduous, sometimes dangerous, inefficient with respect to the life of new refractory material used, and nearly always have necessitated interruption of the continuity of the furnace operations and therefore reduction in furnace production during the period of time required for the repair work. Most of these older methods have involved the replacement of masonry by refractory shapes in the weakened areas. Many attempts have been made to develop a method of patching the burned-out areas by spraying granular refractory material upon old surfaces. While some success has been attained in attempts to renew the grooved, corroded side walls and fettling, and the edges of hearths, there have been no known successful applications of the spraying method in patching the underside of arches of operating furnaces.

The method developed recently at the Clarkdale smelter of the United Verde Branch of Phelps Dodge Corporation, at Clarkdale, Ariz., and described in this paper, has been found to be not only convenient and successful with respect to patching vertical or inclined surfaces, but has met with a marked degree of success in patching the parts of furnace arches that are exposed to flame, the successful result being obtained without interruption or interference with the continuity of furnace operations.† It may be described as a method of renewing the interior refractory surfaces of operating furnaces by pneumatic spraying of an aqueous suspension of finely divided particles of refractory material. It has been used

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* Smelter Superintendent, Phelps Dodge Corporation, Clarkdale, Arizona.

† Patents pending.

successfully for patching the arches, side walls, and uptakes of reverberatory furnaces in particular, which at Clarkdale are used for the smelting of hot calcined sulphide for the production of copper matte and slag. The method, however, is applicable to furnaces of other industries, such as open-hearth furnaces, glass furnaces, and others.

A few years ago a reverberatory furnace in operation at Clarkdale developed a weakness in a part of the furnace uptake. The location of the failure made hot-patching by the usual methods out of the question. The remainder of the furnace structure was evidently in good enough condition for further operation of weeks and possibly months. It was decided, therefore, to try a spray method of patching. A refractory gun manufactured by the Quigley Company was available, and attempts were made to apply a successful patch by spraying. Although the practices applied were makeshift, they sufficed to repair the uptake and prolong the life of the furnace, and the success of this initial operation led to experimentation, out of which has come the method that is the subject of this paper.

THEORY AND PRINCIPLES

It was soon ascertained that any particular type of design of projecting equipment was not an essential factor in the success of hot-patching. The Quigley gun mentioned above was found to be a satisfactory piece of such equipment, but experience showed that other kinds would be satisfactory also, and a projecting apparatus of home manufacture was found to be simpler to use, of greater capacity, and capable of speeding up the work.

One of the greatest difficulties was the designing of a spray pipe that could be inserted into and exposed to the flame of the incandescent furnace interior for the time required to spray the material on the interior surface. This difficulty was overcome by suspending the refractory material in water and blowing the aqueous suspension through the spray pipe, the presence of the large amount of water keeping the spray pipe cool and free from deformation. Thus it was very easy to use a spray pipe of any length desired, and of small diameter, so that one operator could easily and effectively handle the tool. The usual practice at Clarkdale is to use a spray pipe about 20 ft. long, made of standard $\frac{3}{4}$ -in. steel pipe.

Experiment soon demonstrated that in patching the underside of arches only the very finely divided particles of refractory material could be deposited upon the surface to be repaired. Larger particles failed to deposit because of the sandblasting effect and rebound. Furthermore, if many coarser particles were present the sandblasting effect of these particles tended to blast off deposits of the particles that were fine enough to adhere. Thus it became apparent that pulverized refractory material

must be substantially through 200 mesh in size. It was also evident that the pulverized material must contain a considerable portion much finer than 200 mesh.

The essential elements of aqueous suspension and fineness of particles having been demonstrated, the additional factors, such as chemical composition and mixture of powdered refractory materials, were investigated. The optimum mixture depends upon a furnace's performance and the temperature at which it is operating. Variations may be made in consideration of the chemical composition of the material being smelted in the furnace, as well as of the particles that are dusted from the furnace charge and impinge against the interior flame-exposed refractory surfaces. Thus, for repairing the silica arches of the reverberatory copper-matting furnaces, which usually are built with silica side walls and arches, it has been found that pulverized silica containing 96 to 98 per cent SiO_2 is satisfactory, and also that an admixture of a small amount of pulverized fire clay, or pulverized magnesia, pulverized lime or other material, may be used, the amount depending upon the patch durability required at the temperature and other conditions to which it is exposed. As an example, at Clarkdale mixtures of pulverized silica with 2 to 4 per cent fire clay, and as high as 8 per cent, are frequently used; also, mixtures containing similar amounts of lime or pulverized periclase (relatively pure magnesia), or small amounts of flue dust, have been used.

THEORY OF FORMATION OF BOND IN REFRACTORY PATCHES

Petrographic examinations of portions of patched material removed from furnaces after operations indicate that the bonding of the patch material was the result of recrystallization of the quartz into tridymite in the presence of molten fluxes, and it is the interlocking of the tridymite crystals, according to the theory developed, that accounts for the bond formed in the patch itself. Quartz is known to invert in two ways to tridymite; (1) in the presence of certain mineraloids directly to tridymite; (2) first to cristobalite and then to tridymite. Silica brick itself, after a furnace has been in operation for some time, is completely inverted to tridymite in the hotter portions of the brick. By the application of a patch containing finely divided silica with flux such as fire clay or lime, an interlocking bond is obtained between the patch and the original brick by solution and recrystallization of tridymite from the brick and simultaneously from the patch. In actual application of the patch material to the furnace, it is essential that the material be applied in thin layers in order to give time for this bonding action to take place; otherwise, a patch may be built up too thickly, and the contact between the brick and the patch may never attain the temperature at which the recrystallization, with resulting bonding, can take place.

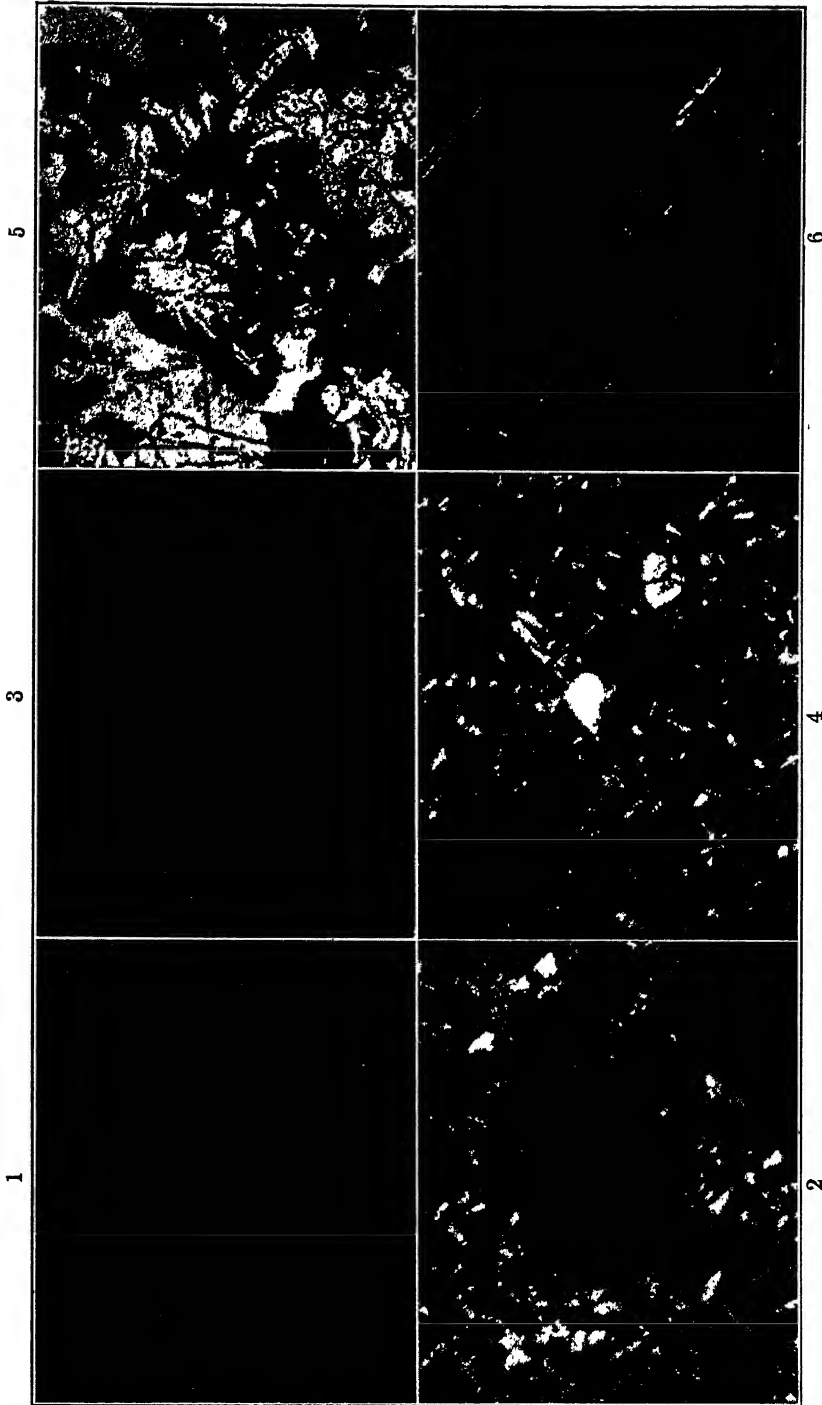


FIG. 1.—CRISTOBALITE OF SILICA BRICK IN PROCESS OF INVERSION TO TRIDYMITE.
 FIG. 3.—TRIDYMITE STRUCTURE OF PATCH MATERIAL WITH QUARTZ (ENCIRCLED) IN PROCESS OF INVERSION TO TRIDYMITE.
 FIG. 5.—TYPICAL TRIDYMITE STRUCTURE OF PATCH MATERIAL AFTER INVERSION HAS BEEN COMPLETED.
 FIGS. 2, 4 AND 6.—SAME FIELDS AS FIGS. 1, 3 AND 5, RESPECTIVELY. CROSSED NICOLS.

Inversion of quartz to tridymite is dependent upon temperature and the presence of certain fluxes, and in the portions of the furnace where the temperatures are relatively low it is necessary to use greater percentages of fluxes than in the hotter portions in order to secure bonding of the patch material.

To support this theory some photomicrographs of thin sections are presented herewith (Figs. 1 to 6). No. 1 shows a section of silica brick that had been in service in a reverberatory furnace, which is composed of cristobalite and tridymite, with the cristobalite apparently in process of inverting to tridymite. No. 2 is the same field as No. 1, but with crossed Nicols. Fig. 3 shows a section of patch material removed from a furnace after operation, with an interlocking tridymite structure and some fracturing quartz. No. 4 shows the same field as No. 3, and discloses wedge twins of tridymite through crossed Nicols. Figs. 5 and 6 show typical tridymite structure after inversion has been completed. Quartz crystals are conspicuously absent in the particular field of these photographs.

A series of determinations of softening and melting points of mixtures of various powdered refractory materials was made in the laboratory by forming such mixtures into the shape of Seger cones and exposing them to flame conditions simulating the flame of operating furnaces as nearly as could be accomplished in the laboratory. This work revealed a considerable variety of mixtures of pulverized silica, with minor portions of other ingredients as mentioned above, which gave promise of producing successful and enduring patches. A number of these have been tried in the furnaces and some have been confirmed by actual practice. On the other hand, the laboratory results confirmed findings that had already been made in actual practice. Thus, several variations in mixtures have been found to be acceptable, although the job of finding the optimum mixture for each particular condition encountered is not considered to be completed. The cost of materials used in the mixture must be considered, as well as the durability of the patch obtained.

DESIGN OF APPARATUS

The projecting equipment consists of two parts, a storage or pressure tank to hold and gradually expel the slurry (aqueous suspension of the pulverized refractory) and a spray pipe with appropriate spray tip to direct the spray of slurry against the surface to be covered (Fig. 7). All of this equipment used at Clarkdale is of local design and construction.

The pressure tank may be any tank with a capacity of about 2 cu. ft. and of suitable construction to withstand 100 lb. pressure. It is mounted on a truck for ease of transportation. For convenience in filling, a funnel of slightly greater capacity is rigidly attached to the tank and there is a gate valve between the two.

High-pressure air may be introduced into the tank in two ways: (1) at the bottom of the tank by means of a pipe inside the tank and extending nearly to the bottom, or (2) at the top above the level of the slurry in the tank. The former is advantageous in causing agitation of the slurry, which helps to prevent settling out of the coarse particles. Pressure at either, of course, will force the slurry out of the discharge opening at the bottom of the tank when the outlet valves are opened. The tank should also have an overflow or pressure-release valve.

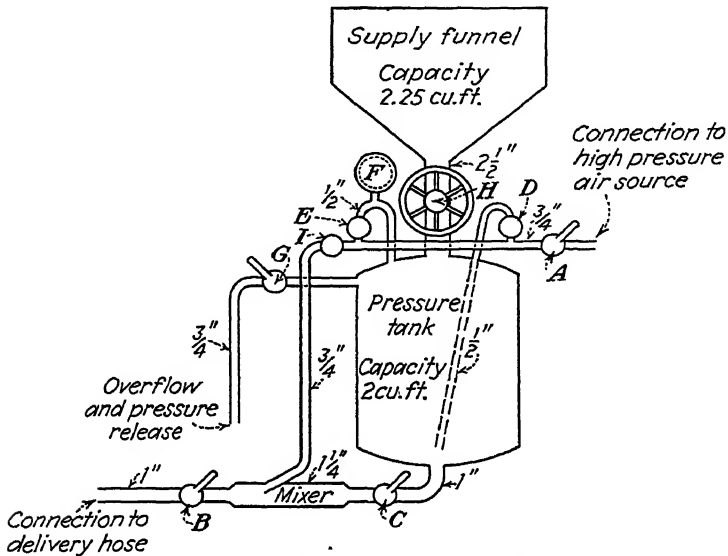


FIG. 7.—REFRACTORY SPRAY GUN.

- A. Plug valve. Always fully opened or fully closed.
- B. Plug valve. Always fully opened or fully closed.
- C. Plug valve set for proper amount of pulp feed. This adjustment is seldom changed.
- D. Gate valve for air pressure to tank, which also agitates the mixture.
- E. Same as D, but pressure is on surface of mixture. Used for thick mixtures.
- F. Pressure gauge.
- G. Overflow and pressure release. Used when filling tank from funnel and for violent agitation of mixture when required.
- H. 2 1/2-inch gate valve for filling tank.
- I. Gate valve for high-pressure spraying air to mixer.

Slurry is expelled from the tank through a hose leading to the spray pipe. A high-pressure air connection is made into this discharge line just before the hose connection, for the purpose of mixing air with slurry to effect proper atomization as the slurry is discharged from the nozzle.

One disadvantage of this equipment is that the operator of the pressure tank has sole control over the kind of spray discharged without usually being able to see the end of the nozzle in the furnace. The nozzleman who is directing the spray is usually out of reach of the valves at the pressure tank and must call directions to the tank operator for

any change desired in the spray. A recent experimental improvement in the gun eliminates this by moving the introduction of the high-pressure air into the slurry stream up to the nozzle itself, with valve regulation of both air and slurry under the hand of the nozzleman at the rear end of the spray pipe.

The spray pipe is a 20-ft. length of standard $\frac{3}{4}$ -in. pipe, with a swivel joint at the rear end for connection to the slurry line (Fig. 8). The forward end has a tip designed to aid in producing a good spray. The tip consists of one or sometimes two couplings joined by a short nipple. The open end is plugged and openings of various designs are cut in the side of the couplings, so that the spray is directed at right angles to the spray pipe. Round, square, triangular and slotted openings have

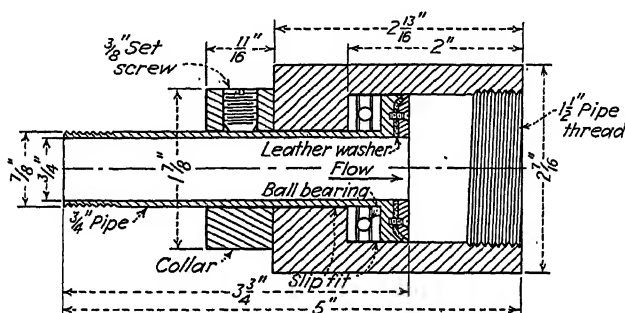


FIG. 8.—SWIVEL JOINT FOR GUN NOZZLE.

been used, the slots being in favor at present. The size, within reason, and the design of the openings, seem to have little effect on the spray, the important item being the proper amount of air. In fact, good results have been obtained by merely bending upward the end of the spray pipe and shaping the discharge opening to a desirable orifice.

Because of the abrasive action of the discharging slurry, the tips wear out rapidly. This is the most serious wear on the equipment. The spray pipe is cooled while in the furnace by the slurry within it.

SELECTION AND PREPARATION OF REFRACTORIES

Because the patch must be as durable as possible and bonded to the old surface as permanently as possible, selection of the proper refractories or mixtures of refractories is dependent upon (1) the chemical composition of the surface to be repaired, (2) temperatures to be encountered, (3) atmosphere in the furnace.

The chemical composition of the surface to be repaired is an absolutely fixed quantity, and the temperature range is also more or less limited by the desire to maintain normal operating conditions at all

times. This means that only the composition of the patch, or the new layer to be joined to the old, can be varied. Obviously it must be properly chosen if fusion is to be effected. In this connection the equilibrium diagrams for the various refractory oxide systems, as well as fusion-point determination of mixtures of suitable composition by means of the standard P.C.E. (pyrometric cone equivalent) laboratory test methods, have been very helpful.

As mentioned, the surfaces to be repaired in the reverberatory furnaces of this smelter are silica brick, which has limited the choice of refractory mixtures to those predominantly siliceous in character. Several attempts were made to deposit a basic patch, largely of bauxite or periclase, because it was believed such a patch might be more durable—that is, resistant to the corrosive fluxing action of FeO and Al_2O_3 of the dust in the furnace atmosphere—but all failed, probably because of the formation of such a fluid slag at the interface that the patch could not be held in position.

Furnace temperatures, however, are not high enough to effect the fusion of pure silica particles in the patch mixture to silica brick without the presence of some fluxing agent. For this reason, if the powdered silica is too pure, minor amounts of various basic materials such as fire clay, lime or periclase are added to the main siliceous constituent of the patch mixture. As a matter of fact, chemical analysis and microscopic examination of the bonded patch indicate that the dust in the furnace atmosphere arising from charging operations and from the combustion of the pulverized coal, acts as a fluxing agent, and at times small amounts of calcine or flue dust have been added to the mixture to secure this reaction.

In addition to being so composed that this bonding by fusion will take place, the mixture of refractories must be regulated so that the patch will be able to withstand furnace temperatures and not melt away. At first it may appear paradoxical that fusion for bonding purposes can be accomplished without melting away of the patch. What we strive for, however, is a mixture that will only partly fuse, or form an extremely viscous slag at the contact zone, which then becomes more solidified as it is protected from the heat by further building up of the patch. Obviously the temperature range within the patch is close and the permissible variations in mixtures are small. At the same time, any great changes in furnace temperature or dusty condition may upset the calculations and dictate a considerable change in mixture.

The atmosphere in the furnace is a factor to be considered in the proper mixture, not only because of the part any calcine dust or coal ash may play in the bonding of the patch but also because it is the purpose of the patch to withstand the corrosive fluxing action of these constituents of the atmosphere at the exposed surface of the patch.

The refractory materials used at this smelter have been obtained from various sources. Examples of satisfactory materials with their approximate analyses are given in Table 1.

TABLE 1.—*Materials Satisfactory for Use in Hot-patching*

Material	Analysis, Per Cent					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Ignition Loss
Victorville ganister.....	97.1	0.8	0.9	0.1	0.1	0.2
Seligman silica.....	94.5	2.8	1.0	0.25	0.25	1.1
Winslow silica.....	96.6	1.3	0.9	0.2	0.4	0.5
Gallup fire clay.....	50.3	30.2	7.6	0.6	0.9	11.4
Periclase.....	4.8	0.5	2.4	2.5	90.0	

Approximate screen sizes of the pulverized materials used at Clarkdale are as follows: +200 mesh, 25 per cent; -200+300 mesh, 25 per cent; -300 mesh, 50 per cent.

The pulverizing is done in the Raymond mills that are used in the preparation of pulverized coal. Any suitable pulverizing mill could be used, and, as a matter of fact, it may be possible that natural deposits of fine refractory material could be discovered and utilized. The Meteor Crater (Winslow) silica that we have used has approached that condition.

PREPARATION OF THE SLURRY

The actual preparation of the slurry is a fairly simple process. The different refractories in proper proportions are mixed with about one-half the necessary water in a concrete mixer near the storage bins. Refractories are carefully weighed and water is measured by a flow meter.

From the mixer the thick slurry is transported in a concrete buggy to the furnace undergoing repairs, where it is dumped into a mortar box through a 4-mesh screen, to remove any lumps that might plug the projecting equipment. Final addition of water to bring the slurry to about 50 per cent solids by weight is made in this mortar box with stirring by a mortar hoe to keep the batch in suspension.

APPLICATION OF THE SLURRY

For maximum speed in applying a patch, four men are needed, as follows: (1) mixer man, (2) laborer to transport thick slurry, (3) pressure-tank operator, (4) nozzleman.

The areas to be patched are made accessible by various working openings. For the arch and drop holes, longitudinal openings about 12 in. high and 2 to 4 ft. long are made in the side walls between the buckstays and just below the skewbacks. For the uptake, openings are

made in the side and end walls at various strategic points, so that the entire surface may be covered. These openings are plugged with plastic mud when not in use.

The small working holes having been opened, application of the patch is started. The firing and other furnace operations are not interfered with during the application of the patch. The pressure-tank operator fills the tank with slurry and regulates the delivery of slurry to the nozzle by proper manipulation of the air and release valves. As soon as the



FIG. 9.—EQUIPMENT IN OPERATION.

spray starts, the nozzleman introduces the nozzle into the furnace and by almost continuous movement of the nozzle sprays the mixture over a considerable area. When the pressure tank is empty, the nozzle is withdrawn, to avoid overheating while the tank is being refilled. Fig. 9 shows the apparatus in action.

For successful deposition of material without excessive loss due to spattering, or rebound, some skill in the proper technique of application is demanded. While we believe that in the most successful application of a patch the formation of a fusion bond starts fairly soon after application, there is still an appreciable period of time during which the patch must be held in place by surface adhesion until this fusion starts. It is here that skill in application plays an important part. In general, the

operator attempts to maintain the proper kind of spray and to keep the surface being covered at the right temperature and covered with the right thickness of material so that as the deposit dries out it will adhere to the brick.

"Proper kind of spray" refers to atomization of the slurry and to velocity of projection. A uniform, steady and fairly divided spray is beneficial, but too great velocity of projection must be avoided, or the spattering loss will be excessive.

In addition to maintaining the proper spray, the nozzle-man must move this spray over the surface being patched at the proper rate to cool the surface down to the point at which adhesion of the mixture to the brick takes place without at the same time applying too heavy a coating. If too thick a coating is applied, part of the deposit is forced off in large flakes as it dries out. In general, it has been found to be good practice to apply thin layers and allow the newly patched area to dry out and become set while working on an adjacent section.

RESULTS

At Clarkdale it has been demonstrated that furnace campaigns of one and one-half years are obtainable with 25 by 100-ft. furnaces smelting at the rate of 1000 tons of solid charge per day. Thus it has been the experience that campaign tonnage of over half a million tons is not unusual.

The cost of this method of patching increases with the age of the campaign. When weak spots first appear they are usually localized, and since patching is confined to such small areas the cost is small. As the campaign continues, the areas requiring patching increase in size, until finally the amount of hot-patching required to maintain the furnace in operation entails an expense that approaches the normal cost of renewing refractories by shutting down the furnace for regular overhauling. Other factors and operating convenience are then to be considered in deciding whether the campaign should be prolonged. Frequently the need of servicing waste-heat boilers and accessory equipment makes it advisable to terminate the campaign.

Cost of patching depends on local conditions, such as the price of powdered refractories, labor, compressed air, etc. The ratio of arch repairing to side-wall repairing is also an important factor. Because of the rebound when patching the underside of an arch, it should be assumed that not more than 20 per cent of the solids sprayed will actually deposit, but in lateral spraying on to side walls the percentage deposited is much greater.

Older methods of hot-patching taxed the physical endurance of those employed in the task, and frequently could not be humanly tolerated.

The present method extends the field of hot-patching and imposes upon the repairmen a relatively easy and safe task.

ACKNOWLEDGMENTS

The process described was successfully developed because of the cooperation and enthusiasm of a loyal staff. While all concerned were helpful, contributions by the following named to the development of the process or to this paper should be especially acknowledged: M. G. Fowler, metallurgist, for considerable advice and direction; F. X. Mooney, general reverberatory foreman; F. W. Winkler, head mason, and Melvin Mounts, mason, for practical application; P. S. Geshell, for the petrographic study; and H. D. Crawford, for laboratory test data and assistance in the actual preparation of this paper.

DISCUSSION

L. L. McDANIEL.*—The Clarkdale hot-patching method has been in use at the Douglas smelter for the past 18 months, the method followed being essentially the same as that described by Mr. Kuzell.

Before adopting the hot-patching method we were obliged to make arch repairs in the firing section about every four or five months, but since using this method we are able to plan on double the arch life before shutting down to repair the furnace. We have not as yet determined the maximum length of campaign possible with hot patching, or the point at which it is more economical to shut down for a repair than to continue hot patching.

Hot patching is rather simple to perform once the workmen have acquired the necessary skill in manipulating the spray pipe, to obtain a satisfactory deposit of the finely ground silica on the hot arch or side wall. When a furnace is finally shut down for repairs, some parts of the underside of the arch are so well cemented together as to form a monolithic section, which is not easy to bring down.

* Phelps Dodge Corporation, Douglas, Arizona.

M. W. KREJCÍ.*—Mr. Kuzell and his associates are to be congratulated on the very ingenious method that they have perfected. The longer life of furnace roofs in the smelting zone has materially reduced repair costs.

It brings to mind experiments made by H. F. Easter, superintendent at Hayden, Ariz., about 10 years ago, on the center-feed furnaces at his plant, during the Carson patent litigation. Mr. Easter found that he could lengthen the life of the furnace roofs in the smelting zone by injecting live steam into the furnaces, aimed at the roofs, during charging of calcines. The calcine fines adhered to the roof and formed a protective coating. By the time this smelted off, it was time to charge and repeat the operation.

A short time later most of the smelting plants of the country were shut down by the depression. Very little experimenting was done by most of the smelting companies after resumption, because of the very low price of copper. Mr. Kuzell's method has the advantage of the use of more highly refractory material than the method of Mr. Easter, and of not having to do it as often.

* Worcester, N. Y.

Transportation of Molten Blister Copper by Rail from Smelter to Refinery

BY FREDERIC BENARD,* MEMBER A.I.M.E.

(New York Meeting, February, 1938)

PRIOR to 1936, the Ontario Refining Co. received all incoming blister copper from The International Nickel Company's smelter in the usual form of 460-lb. cakes, or slabs. These were received in open cars in lots of 250 pieces. At the refinery the cakes were unloaded onto narrow-gauge cars, for convenient handling and pickup by charging cranes.

In March 1936, an investigation was started on the feasibility of transferring converter copper in the molten state from the smelter to the refinery anode furnaces, a distance of $1\frac{1}{4}$ miles.

Although common in steel practice, the transportation of blister copper in this form had not previously been attempted and a preliminary study of the various factors involved was therefore necessary. For this purpose, a series of experiments was made in which molten copper, removed at different stages during the furnace cycle, was held in a small portable holding furnace. This vessel was essentially a refractory-lined steel cylinder provided with ports for filling and emptying, heated by an oil burner. Dimensions of the steel shell were 3 ft. 10 in. diameter by 7 ft. 3 in. long, and thickness of refractories depended on the design and combination used for the particular experiment. The vessel was filled with approximately $2\frac{1}{2}$ tons of copper at a predetermined temperature, the lining having been preheated to a definite point by means of an oil burner. All openings were well luted and temperature readings were made every 15 min. by means of an immersion-type thermocouple. In this manner the rate of heat loss resulting with different refractory design could be developed. The ratio of exterior surface to weight of metal was taken into consideration in comparing the experimental results with what might be expected for a full-sized unit, and observations were also made on type and degree of slag accretion. It was not possible to get as much information on this latter point as desirable, but all evidence showed that the problem would be control of slag build-up rather than attack on refractories.

From the information derived, and in consultation with the engineering staff of the supplying company, an order was placed for the first

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* Plant Manager, Ontario Refining Co., Ltd., Copper Cliff, Ont.

portable holding furnace, or hot-metal car. This unit arrived and went into service in July 1936. Subsequently, three more cars of slightly modified design were ordered, and in August 1937, with four cars in service, operations were placed on an all hot-metal basis.

CONSTRUCTION OF CARS

The new type of car is shown in Fig. 1. The unit consists essentially of a cylindrical ladle with conical ends mounted by means of trunnions

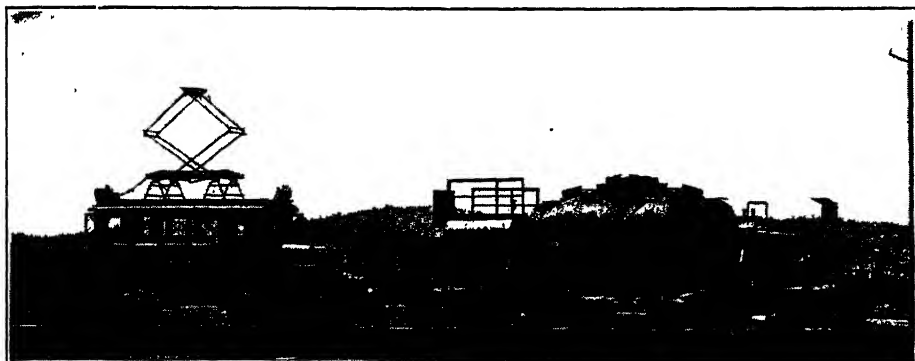


FIG. 1.—HOT-METAL CAR.

and bearings on special car trucks. One of the trunnions is geared through a speed reducer to a 25-hp. motor, which permits rotation for emptying. The ladle shell is constructed of 1-in. steel plate with riveted joints; the length of cars 2, 3 and 4 is 18 ft., and the diameter at mid-section 9 ft. 1 in. When the refractory lining is in place, the carrying capacity is approximately 300 cu. ft., equivalent to about 70 tons of molten converter copper. The mouth of the ladle is 2 by 3 ft., and is located midway between the ends. In addition, burner ports are provided for use when heating up a cold car or holding a charge under heat. Auxiliary equipment consisting of a compressor together with oil and air tanks, to permit burner operation in transit, was provided on the first car. This feature was excluded on succeeding units, in the light of further experience. The whole assembly is carried on four four-wheel trucks equipped with roller bearings, which make for maximum mobility. Standard air brakes are controlled from the locomotive. An unlined car after assembly weighs 195,000 lb.; after lining, approximately 275,000 lb.; indicating a refractory weight of 80,000 pounds.

The lining proper, which is 18 in. thick, consists of 9 in. of magnesite backed up with two $4\frac{1}{2}$ -in. courses of fire clay. Next to the shell, $1\frac{1}{2}$ in. of insulating cement is used to bring the rivet heads level. A majority of the shapes used are special arch wedges, standard sizes being mainly restricted to the ends. In lining No. 1 car, the first course of fire clay

next to the insulating cement in the upper half of the shell was replaced by insulating firebrick; for the course next to the metal, unburned magnesite was employed. In succeeding cars no insulating brick was used and special burned magnesite is being studied in comparison with the chemically bonded variety. The general lining arrangement for cars 2, 3 and 4 is shown by two sections in Fig. 2.

METHOD OF OPERATION

Two types of molten blister are received from the smelter. That produced from matte from the Orford process of separating copper and

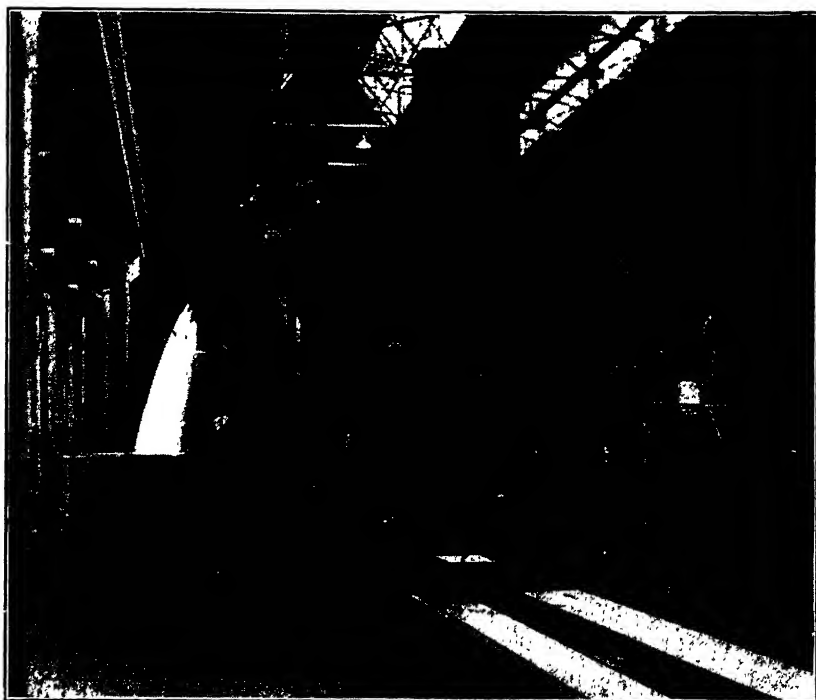


FIG. 3.—CAR DISCHARGING INTO LAUNDER.

nickel is highly oxidized. The other, resulting from the reduction of a high-grade copper concentrate has a comparatively low oxygen content. Both contain varying amounts of sulphur. The two grades are designated locally as O.P. and N.P. copper, respectively.

Before a newly lined car is filled, or when a car has been out of service for some time and grown cold, lining temperature is brought up to approximately 2200° F. by means of oil burners. In the smelter converter aisle, copper is transferred from converter to car by means of 20-ton ladles. Time of filling is variable, depending upon length of converter cycle. When the car is full, about 50 lb. of charcoal is thrown on top of the bath, to prevent freezing around the ladle mouth.

The loaded car is hauled about $1\frac{1}{4}$ miles to the entrance of the refinery anode building, by an electric locomotive. No men other than the regular locomotive crew are required in transportation movements. At the anode-furnace building the car is picked up by an electric winch and endless cable device, which permits spotting at the desired furnace. The power cable to the tilting motor is plugged into a convenient outlet and pouring commences.

Emptying the car is completed in 6 to 8 min. The molten blister flows from the car into a spoon-shaped launder (Fig. 3), from which it runs into the 300-ton furnace. During pouring, lumpy slag tending to obstruct the flow in the ladle mouth is skimmed into the stream by an operator from an elevated platform over the furnace. When empty, the car is immediately moved away from the furnace and the launder basin is drained by elevating it with a crane.

Before the car ladle is turned back to an upright position, it is examined for defective brickwork and any lumps of slag that have not come out in the metal stream are removed with a rabble. The car is then moved out of the building, picked up by the locomotive, and returned to the smelter. The time required for a cycle consists of approximately 1 hr. for transportation between refinery and smelter, plus 20 min. for handling in the anode department. The filling period is a variable, dependent on smelter conditions.

HEAT LOSSES IN TRANSPORTATION

As previously noted, the first hot-metal car was provided with oil-burner equipment for use in transit. Experience proved, however, that rate of heat loss was not great enough to necessitate this feature. Temperature of O.P. copper as charged to the car averages about 2400° F. and that of N.P. copper about 2300° F. The average drop during transit between smelter and refinery is approximately 55° F., and the loss when holding a charge without external heat is roughly 60° F. per hour. It is possible, therefore, to hold a charge without burners for 3 to 4 hr. In actual practice, it is preferred to offset heat loss by operating an oil burner if a condition arises causing delay in handling. This eliminates the possibility of undesirable skulling in the car. During the summer months, the outside shell temperature averages 350° F.

SLAG BUILD-UP IN CARS

Earlier investigations were confirmed during the preliminary operating period of No. 1 car when it became apparent that the slag problem was one of accretion rather than erosion or attack of refractories. Several methods of cleaning out built-up material were investigated, and these showed that ordinary heat-treatment was useless because of the extremely

refractory nature of the slag. It became apparent that chemical combination with a reducing constituent was required. This led to the matte wash-out treatment, in which a car is treated at the smelter with charges of low-grade furnace matte. The procedure is as follows:

The car, when taken out of service, is brought up to a good heat with an oil burner inserted through one of the ports. Approximately 10 tons of matte at 2000° F. is poured into the car and a green pole is inserted. A strongly reducing flame is kept on the burner and the pole creates a vigorous agitation. This operation is kept up for 4 hr., during which time the car is rotated from side to side at frequent intervals, to bring the upper surfaces in contact with the matte. At the end of this period the charge is run out and the treatment repeated. This is done until the slag is almost completely removed, which takes approximately 48 hr. The temperature of the matte when drained out has risen to 2400° F.

Present practice is to divert cars for matte wash-out treatment after every 50 to 60 trips. The increase in tare weight due to slag build-up is somewhat erratic, varying with trip frequency, et cetera.

During investigation of this phase of operation, it was found that the conical ends of No. 1 car built up very quickly. Accordingly, cars 2, 3 and 4 have less conical section and an increase in the diameter of the cylindrical portion. The simplified shape has made these cars easier to line and greatly facilitated slag removal.

CHANGES INVOLVED FOR HOT-METAL OPERATIONS

The operation of the hot-metal cars has brought about changes in smelter and refinery practice in handling blister. Previous to the time of transportation of molten blister, the converter copper at the smelter was charged to two 150-ton reverberatory coal-fired holding furnaces. These, when full, were skimmed free of slag and were then poled to give cakes with a flat set, which would pile satisfactorily for transportation. The charges were then cast on straight-line casting machines.

These two furnaces have been eliminated, although the casting machines have been retained so that in case of interruption of the hot-metal car service the converter charges can be cast directly into cakes by means of ladles.

At the refinery, it was necessary to provide means for bringing the cars into suitable proximity to the anode furnaces. This was done by continuing the outside broad-gauge track into and for the length of the anode-charging aisle paralleling an existing narrow-gauge track used under the old system. The latter is retained to permit charging anode scrap and other secondary material. The broad-gauge track is carried on a concrete foundation 22 in. above floor level. An endless cable driven by an electric winch passes down a trench in the center, and by a simple attachment hot-metal cars are moved to the desired position.

The launder into which the blister is poured is placed in position before the car is spotted in front of the furnace. It is mounted on four wheels that run on a short track, which crosses the narrow-gauge track at floor level and at right angles to it. The trough enters the furnace through the door opening nearest the burner end. Movement of the launder toward and away from the furnace is provided so that the position can be changed to agree with that of the car lip.

The basin of the launder holds about three tons of molten blister. It becomes filled with frozen blister and slag after being used for emptying about 10 cars, necessitating a replacement. The frozen material is removed from the used launder and any necessary repairs are made to the lining.

FURNACE TREATMENT OF MOLTEN BLISTER CHARGES

The treatment of molten metal direct from the converters, as against the remelting of blister cakes, has naturally modified previous anode-furnace refining practice. These changes are shown in Table 1, on the basis of 300-ton charges.

TABLE 1.—*Comparison of Furnace Cycle for Blister Cake and Hot Metal*

Process Data	Blister	Hot Metal
Charging, hr.....	2	15
Melting and skimming, hr.....	14	5
Flapping, hr.....	1½	
Poling, hr.....	2½	3
Casting, hr.....	3½	7
Complete cycle, hr.....	23½	30
Percentage of slag.....	2	5

During the filling period, sufficient coal is burned to keep the charge at approximately 2250° F. As soon as the metal level is high enough, skimming commences, the amount of slag being more than double that removed from a cake charge. This, of course, is because the charge contains varying quantities of converter slag and also has a high oxide content.

Furnace charges normally consist of one-third Orford-process copper and two-thirds copper originating from concentrates. This gives an oxygen content of 0.90 per cent after skimming without additional flapping. Any sulphur in the bath is oxidized during the skimming operations. The poling period is somewhat extended on molten blister charges, owing to the higher initial state of oxidation.

Slag removed from each charge is sampled and returned to the smelter, where it is reverted to the process. Tank-house scrap and other secondary material is "hot-charged" during the casting period, thus utilizing any excess heat in the charge after poling.

When blister cakes formed the charge, about 42 furnace days was required to handle the present production, and with two furnaces operating both furnaces cast on the day shift. The slightly less than 24-hr. cycle combined with double casting wheels enabled this to be done easily with a single crew.

On hot-metal operation it is obviously essential that there be a minimum delay in emptying the cars to avoid the use of oil burners and permit prompt return to the smelter. Therefore it is necessary that there always be a furnace available at the refinery to receive molten blister, and this is accomplished by operating two furnaces continuously on a staggered cycle. The third furnace is kept in good condition for replacement service as repairs become necessary.

As the furnace cycle has been extended to 30 hr., it is necessary to have the crew on each of the three 8-hr. shifts capable of handling all phases of the operation. This is facilitated by using one casting wheel only when taking out a charge. The extended casting time is necessary in order to keep the periods when the furnace is "open" and "closed" equal in length. On the shifts during which no casting occurs, the casting crew is utilized in other work.

The reason the furnace cycle has been extended from 24 to 30 hr. is explained by the fact that during the filling, or "open," periods the refinery units are actually operating as holding furnaces.

WEIGHING AND SAMPLING OF MOLTEN BLISTER

The weight of molten blister carried in each hot-metal car trip is not determined. It is not feasible to determine the weight of the blister content accurately, because of the variable quantity of slag charged to each car along with the blister. However, at times it is desirable to know the weight of the contents of the cars and also their tare, in order to check slag build-up. These weights are obtained by placing each pair of supporting trucks on the scale separately and combining the two readings. This is done on a railway platform scales of 125 tons capacity.

The contents of each hot-metal car is sampled by cutting the stream during the emptying operation with a steel sample ladle and shooting in a container of water set beside the launder.

Settlement for blister received by the refinery is no longer made on blister assays, but on anode weights and assays. Every fourth rack of anodes that is cast is taken for sampling, each anode of which is drilled by the continuous template method.

BENEFITS OF HOT-METAL CAR OPERATION

The advantages of transporting converter copper direct are shared by both smelter and refinery. At the former, there is eliminated the operation of two 150-ton holding furnaces and the subsequent casting

process. At the refinery, the unloading and handling of blister cakes is replaced by the simple emptying of hot-metal cars, the economy of which is obvious. Saving on fuel because there is no melting down of cold charge is slightly offset by the longer furnace cycle, but the cost of fuel per unit charge is steadily decreasing as furnace crews become more proficient in the new technique.

It is not now necessary at any period of the cycle to use as intense a heat as formerly was required, notably during the melt-down stage. This will definitely lengthen the life of refractory linings, especially the roof. Extended service may also be looked for from furnace bottoms, no longer subject to the shock of heavy loads of solid charge.

Possible bottom erosion where the stream of molten metal impinges when an empty furnace is being filled has been forestalled by the use of magnesite-brick bottoms, plus continuous fettling at this area. These bottoms are in perfect condition after use for several months, and appear to be destined for a life of many years.

ACKNOWLEDGMENT

The writer wishes to make due acknowledgment to Mr. Donald MacAskill, President of the Ontario Refining Co., for his interest and support in this development, and to those members of the staff who have rendered assistance.

An Investigation into Anode-furnace Refining of High-nickel Blister Copper

BY FREDERIC BENARD,* MEMBER A.I.M.E.

(New York Meeting, February 1938)

THIS paper constitutes a preliminary report on experimental work done to date on the anode-furnace treatment of blister copper containing relatively high percentages of nickel. The investigation has not been completed but results obtained to date are considered of sufficient interest to warrant publication.

Blister copper treated by the Ontario Refining Co. originates from the Copper Cliff smelter of The International Nickel Company of Canada, of which the former is a wholly-owned subsidiary. The blister as received contains from 0.50 to 1.50 per cent Ni, and in this respect differs from that treated by other refineries on this continent. During the anode-furnace treatment, only a portion of the nickel content is removed, and of the amount remaining in the anodes a varying percentage is found in the anode slimes. This necessitates a more extensive treatment than ordinary nickel-free material. Sometimes it is necessary to repeat roasting and leaching operations several times before the nickel content is low enough to permit the slimes to proceed to the doré furnace. This, besides increasing treatment charges, causes greater selenium stack losses and involves a longer tie-up of precious-metal values. Therefore this investigation was undertaken with the aim of determining the factors influencing the diversion of nickel into the anode sludge.

From experience it was known that by keeping the nickel content of anodes at 0.55 to 0.60 per cent maximum a relatively satisfactory slime resulted. One avenue of attack therefore was developing improved elimination in the anode-furnace treatment so that the anode content mentioned above was not exceeded. Another angle was to improve the solubility, during electrolysis, of the nickel constituent in the anodes, thus decreasing the percentage diverted to slimes. It may be mentioned here that nickel dissolving electrochemically and entering the electrolyte presents no difficulty from a treatment standpoint.

Both of these approaches were studied and are discussed separately below.

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ELIMINATION OF NICKEL IN THE ANODE FURNACE

Fire-refining methods, as far as is known, have not been successful in eliminating more than small quantities of nickel from copper. Schnabel¹ mentions cases of fairly complete elimination in the slag formed by repeated oxidation and reduction of the bath. Stahl² has proposed the addition of iron scale to the bath, resulting in the formation of nickel ferrite, which is slagged off. Such procedures are not practical even if capable of accomplishment.

Although possessing similar values for heats of formation of their respective oxides, nickel and iron are entirely unlike in regard to their formation of slags. This leads to a belief that in ordinary furnace refining a nickel-oxygen compound is formed, which is soluble in copper and therefore does not rise to the surface and enter the slag. Observations made in the work described below all tended to confirm this view.

Two types of blister are received by the refinery; one obtained from converter treatment of copper sulphide separated from nickel by the Orford process, the other resulting from the treatment of a high-grade copper concentrate. The former is designated locally as O.P. copper, the latter as N.P. (New Process).

As described elsewhere,³ all copper is now transferred from the smelter converter department to the refinery anode furnaces in the molten state. O.P. copper carries from 0.65 to 1.50 per cent Ni, and N.P. from 0.50 to 1.00 per cent. In general, the converter treatment provides the desired oxygen content of 0.90 per cent and further flapping is unnecessary except to blow down the slag. The latter is skimmed off, the bath is covered with coke and poled to a flat set. This results in the elimination of virtually all sulphur and from 15 to 20 per cent of the nickel. A series of experiments was first carried out to determine whether the percentage of nickel slagged off could be increased by continuing oxidation up to the point of 1.00 per cent oxygen. Only a small increase in slag quantity resulted, and the actual improvement in nickel removed was too slight to be of economic benefit.

Further trials were made over a considerable period, during which the bath of anode copper was saturated with cuprous oxide at a temperature of about 2300° F. and then allowed to cool to approximately 2100° F. This drop in temperature caused a precipitation of molten cuprous oxide, which carried with it 10 to 15 per cent of the total nickel present. This quantity again was not great enough to warrant spending the additional time required to carry out the procedure.

Prior to and during all experimental work on nickel elimination, careful records had been accumulated on the behavior of various lots of anodes during electrolysis. In tabulating these data, two general observations became apparent: (1) the proportion of the anode nickel content

¹ References are at the end of the paper.

diverted to slimes increased sharply with rising percentages of nickel in anodes; (2) although this was true for the great majority of cases, there were frequent isolated exceptions. The general relationship between nickel in anodes and slimes produced is shown in Table 1.

TABLE 1.—*Nickel in Anodes and Slimes*

Production No.	Nickel, Per Cent		Per Cent of Total Nickel in Slimes	Pounds Nickel in Slimes per Ton Corroded Metal
	In Anodes	In Slimes		
187	0.46	3.2	2.6	0.24
199	0.56	15.7	8.3	0.93
367	0.62	22.6	11.3	1.39
160	0.77	31.2	21.7	3.34

The exceptions referred to indicated some variable which under certain conditions greatly improved the electrolytic solution of the nickel constituent. This appeared worthy of investigation and as tank-house operating conditions are very uniform it was logical to look first for compositional variations in the anodes themselves. Spectroscopic, microscopic and chemical analyses were made, which revealed little or no segregation of metallic constituents but offered a lead from the standpoint of oxygen content.

The next step was to prepare small experimental anodes from regular furnace productions with the further step of chemical deoxidation. The anodes so produced were corroded under conditions identical with those obtaining in regular practice and the slimes resulting were examined for nickel. The results are shown in Table 2.

TABLE 2.—*Deoxidized Anodes*

Lot No.	Nickel, Per Cent		Per Cent of Total Nickel in Slimes	Deoxidant
	In Anodes	In Slimes		
1	0.46	0.38	0.50	Phosphorus
2	0.80	1.07	0.60	Phosphorus
3	0.48	2.22	1.80	Silicon

The exceptionally low nickel content of the slimes tended to confirm the theory that this was related to the oxygen content of the anode. Small amounts of residual deoxidant were found in the slimes but there was no evidence that the increased solubility of nickel was due to formation of compounds with the former. At this time a series of oxygen determinations was made on regular anode productions cast from charges poled to the normal flat set as indicated by the block sample taken before casting. The oxygen was determined on drillings by igniting in hydrogen and applying corrections for sulphur, selenium and tellurium. Slight

errors may have been introduced but the accuracy was satisfactory for the purpose involved. The results showed that the oxygen content of regularly cast anodes varied between 0.10 and 0.30 per cent.

The cause for such wide variation in the oxygen of anodes all poled to a standard "set" is unknown at this time but is thought to be due to the variable effects of poling produced by the impurities in the charge.

Several experiments were next made to examine the effect of varying oxygen content in full-sized anodes in regular tank-house operation, the range covered being 0.04 to 0.26 per cent. Unfortunately, it was not feasible at this time to secure a constant percentage of nickel but in general the observed trend was supported. The lower range oxygens were secured by carrying the poling operation past the flat-set stage to a high or medium crown set, as indicated by the control-block sample. Anodes from these charges were afforded additional protection in that the launder and ladle were well covered with charcoal.

Poling the charge to a medium crown set did not appreciably affect the set on the anodes. However, when poling was prolonged to the point of a high crown set, it was observed that high set areas from 2 to 6 in. in diameter occurred in the anodes toward the last of the casting period.

The high range oxygens were produced either by blowing air on the launder stream or casting before the normal poling operation was completed.

Full tanks of the various anodes so produced were charged to the tank house, the slimes collected separately for weight and analysis. The results are summarized in Table 3.

TABLE 3.—*Effects of Oxygen and Poling on Anode Nickel Entering Slimes*

Production No.	Treatment	Anode Nickel, Per Cent	Anode Oxygen, Per Cent	Slimes, Lb. per Ton Corroded Anode	Slimes Nickel, Per Cent	Per Cent of Total Nickel in Slimes	Slimes, Lb. of Nickel per Ton Corroded Anode
288-2	Air on launder	0.71	0.23	10.4	30.0	22.0	3.12
288-1	Poled to flat set	0.68	0.14	8.7	20.7	13.3	1.81
158-1	Poled to low set	0.54	0.26	8.9	18.3	15.1	1.62
158-2	Poled to medium crown set	0.55	0.04	7.6	7.2	5.0	0.55
298	Poled to high crown set	0.61	0.06	12.0	2.6	2.6	0.31
203	Poled to medium crown set	0.65	0.07	8.3	10.2	6.4	0.84

CONCLUSION

After operation for several months on low-oxygen anodes, experimental results have been satisfactorily confirmed. In addition to the

effect on slimes composition, the amount of copper chemically dissolved in the tank house has been reduced to a point where inside liberator tanks are no longer required, and in general the uniformity of corrosion has been materially improved.

While it is felt that the data are insufficient to permit an exact explanation at this time, it would appear that the oxygen content of high-nickel copper anodes has an important bearing on subsequent behavior during electrolysis with particular reference to slimes composition and electrolytic solution. It is along this line that the investigation is being continued.

ACKNOWLEDGMENT

Acknowledgment is made to the members of the staff that aided in the preparation of this paper.

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2. W. Stahl: Slagging of Nickel in Copper Refining with Formation of Ferrites. Translated from *Metal und Erz* (1931) No. 3.
3. F. Benard: Transportation of Molten Blister Copper by Rail from Smelter to Refinery. See page 56, this volume.

Recovery of Gold from Balbach-Thum Slimes at Copper Cliff, Ontario

BY FREDERIC BENARD,* MEMBER A.I.M.E.

(New York Meeting, February, 1938)

THE treatment of Balbach-Thum slimes at Copper Cliff by the Ontario Refining Co. is of interest because it differs considerably from methods usually employed for the recovery of fine gold from parting-plant slimes. Owing to the comparatively high percentages of palladium and platinum, wet methods are used to remove the greater proportion of these metals before electrolytic refining in the Wohlwill cells.

THE PLANT

The platinum-metals department, Wohlwill room, and gold-melting room extend along the north side of the silver refinery and are separated from the parting plant by a glass partition (Figs. 1 and 2).

The platinum-metals department resembles a laboratory built on a large scale, with the various pieces of equipment laid out on terraces to facilitate handling. Because of the corrosive nature of the solutions, chemical stoneware is used throughout. Elevation of acids is accomplished by means of Mariotte bottles.

On the top level are three steam-jacketed stoneware kettles of 50-gal. capacity, also a packed tower. One kettle is used for digesting the slimes while the remaining kettles are used for precipitating the gold. The dissolver is equipped with a treated concrete hood, which is connected to the flue system. Gases are drawn off through the packed tower by means of a 6-in. stoneware exhaust fan. A 15 per cent solution of sodium carbonate is continually circulated through the tower.

On the intermediate level are two suction filters, one for removing silver chloride and the other for the gold sand. The filter medium consists of an asbestos pad covered with a filter paper on which is a layer of twill.

On the bottom level are two rectangular cementation tanks, 24 by 48 by 24 in. deep, and a suction filter used for removing the platinum-metal concentrates. The circulating pump for the packed tower is also here. Suction is provided by a vacuum pump having a capacity of 8 cu. ft. at 20-in. vacuum.

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Adjacent to the platinum-metals department is the Wohlwill room, which contains a battery of six cells, a set of rolls for fabricating starting sheets, and a stoneware drier for cathodes. The Wohlwill cells are of white porcelain $10\frac{1}{2}$ by $10\frac{1}{2}$ by 12 in. deep inside, and are heated by individual hot plates. A cell consists of two anode rods and three cathode rods, on each of which are suspended three anodes and three starting sheets, respectively. Electrode supports are made of silver. Anodes, which measure 9 by 3 by $\frac{3}{8}$ in. and weigh approximately 70 troy ounces,



FIG. 1.—PLATINUM-METALS DEPARTMENT.

are cast with a hole in the top and are hung from the electrode supports with silver hooks. Cathode starting sheets are strips of fine gold 12 by $2\frac{1}{2}$ by $\frac{4}{1000}$ in. thick. The end of the starting sheet is turned and punched to form a loop, which is threaded on the cathode rod.

Direct current is supplied by a motor-generator set of 200-amp. capacity at 1 to 12 volts. The cells operate at 175 amp., which is equivalent to a density of 100 amp. per sq. ft. Voltage drop is 2 volts per cell.

The electrolyte is a solution of gold chloride containing 90 to 100 grams of gold and 100 grams of free hydrochloric acid per liter. The electrolyte is agitated by air.

The gold-melting room is on the other side of the Wohlwill room. It contains an oil-fired crucible furnace and the necessary anode and bullion molds.

OPERATION

The parting-plant slimes are removed from the cell (Fig. 3) in the muslin lining of the cell basket, by gathering together the corners of the muslin to form a bag. After the entrained electrolyte has been allowed to drain, the bags are charged five at a time into a 20-in. rubber-lined centrifuge of the supported type, where they are washed with hot water. After drying in the centrifuge, the slimes are scraped from the bags into a steel box and transferred to the platinum-metals department.



FIG. 2.—BALBACH-THUM CELLS, PARTING PLANT.

A typical analysis of the washed slimes is: Au, 22.68 per cent; Ag, 32.99; Pt metals, 23.80; Cu, 1.75.

Treatment is carried out on the batch system and a normal charge to the dissolver is as follows: slimes, 54 kg.; muriatic acid, 113 liters; nitric acid, 4.5 liters. In order to avoid an excess of nitric acid, which would prevent complete precipitation of the gold, great care must be exercised in the addition of slimes and acids. Half the muriatic acid is run into the dissolver and heated to 60° C. by careful injection of low-pressure steam. Slimes are then added slowly in small amounts, to avoid too violent a reaction. The solution is stirred with a wooden paddle after each addition. Because there are sufficient nitrates in the slimes, no nitric

acid is required at this stage. When no reaction occurs on the addition of a small amount of slimes, half the remaining muriatic acid is added and the temperature increased to 85° C. Nitric acid is then added in small amounts (150 to 200 c.c. at a time) and the solution is stirred after each addition. This is continued until all reaction ceases. The remainder of the muriatic acid is then added. The temperature is checked and if found low it is brought up to 85° C. again by injecting steam. The charging of slimes is continued until complete, and nitric acid is added in the same manner as before until all reaction ceases.

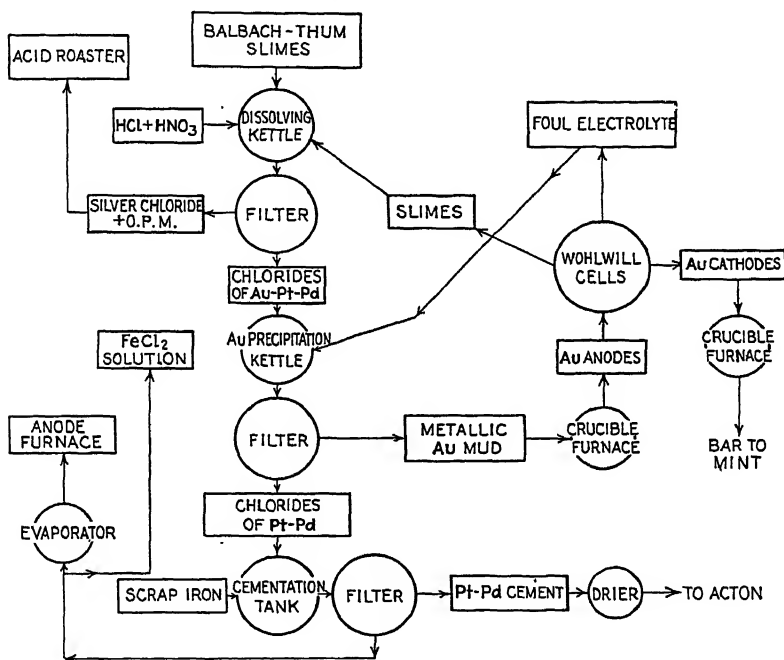


FIG. 3.—FLOWSHEET FOR TREATMENT OF SLIMES.

An average batch requires approximately 3 hr. for dissolving. The charge is then stirred every $\frac{1}{2}$ hr. for a period of 5 hr., during which time the temperature is maintained at 85° C. This method of digesting is effective in dissolving practically all the gold, platinum and palladium, and precipitating the silver as silver chloride.

The charge is allowed to settle and cool for 16 hr. and is then filtered. The silver chloride residue is thoroughly washed with hot water, and, after roasting with sulphuric acid, the converted silver sulphate is charged into the doré furnace. The clear filtered solution is elevated to the precipitating kettles and after the acidity has been adjusted to 65 grams per liter HCl, the solution is diluted with water until a specific gravity of 1.140 is obtained. Temperature is brought up to 40° C. and saturated

ferrous chloride solution is run in with constant stirring until all the gold is thrown down. When the end point is reached—this is indicated by a change in the color of the solution from brown to black—a slight excess of ferrous chloride is added, and after vigorous stirring the charge is allowed to stand for 18 hours.

After testing for complete precipitation of the gold, the charge is filtered. The precipitated gold, being fairly granular, is readily filtered and washed. It is then charged into a No. 20 graphite crucible, melted and cast into anodes. The anodes assay approximately 995 fine.

The electrolysis in the Wohlwill cell takes about 20 hr. and no attempt is made to secure a smooth deposit. Anode scrap is about 20 per cent. Cathodes that weigh 35 to 50 troy ounces are melted in a graphite crucible and cast into 500-oz. bars. The average fineness is 999.8+.

The clear gold-free solution, plus wash water, is charged into the cementation tanks and the platinum metals are thrown down with scrap hoop iron. Complete cementation requires 16 hr. The residue is filtered off on a suction filter, washed with hot water and then with dilute muriatic acid, to remove basic iron salts, and finally with a dilute sodium carbonate solution, to neutralize any free acid that may be present.

The washed platinum-metals concentrate is dried in Pyrex dishes for 20 hr., then ground in a ball mill, to pass 120 mesh. After sampling; the concentrate is packed in steel drums for shipment to the precious-metals refinery at Acton, England. As shipped, the finished concentrate contains approximately 80 per cent platinum metals.

The solution from the cementing process is practically saturated with ferrous chloride but may contain traces of silver, gold and the platinum metals. The excess over that required for precipitation of gold in the next batch is evaporated in cast copper kettles, which are set in an oil bath heated with steam coils.

The crystallized ferrous chloride is charged into the anode furnace for recovery of the precious metals; a representative analysis of the crystallized salts is: Ag, 0.63 oz. per ton; Au, 0.009; Pt, 0.18; Pd, 0.40.

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The writer wishes to acknowledge assistance rendered in preparing this paper by R. H. Waddington, assistant plant manager, and H. A. MacDougall, in charge of technical control, Ontario Refining Co., Copper Cliff, Ontario.

Treatment of Speisses and Drosses as Produced in Lead Smelting

By R. A. PERRY,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

A speiss is an artificial arsenide, sometimes an antimonide, formed in lead smelting, smelting of oxide copper ores, and in some lead-refining operations. The production of speiss is closely allied with the amount of arsenic and metallic iron in the blast-furnace charge, while dross is produced mostly from the copper and sulphur, with varying amounts of antimony, arsenic and nickel.

Most speiss is essentially an iron arsenide containing some sulphur, copper and nickel, if these elements are present in the furnace. The recent introduction of the soda treatment of lead drosses has produced a speiss high in copper.

Speiss is not miscible to any extent with molten copper, lead, matte or slag. Miscibility increases with temperature. This property of the speiss is clarified in the latter part of this paper. Most speisses are produced in conjunction with matte and their sulphur content points to the solubility of matte in speiss.

Some plants have insufficient speiss to warrant separate treatment. When arsenic is high in the blast-furnace charge, there may be sufficient speiss to tap separately from the first settler.

ARSENIC

From the foregoing, it is obvious that a study of the treatment of speiss would not be complete without consideration of arsenic. Inasmuch as perhaps 90 per cent of the blast-furnace feed may be sinter, a

definite knowledge of the properties of arsenical ores and compounds that go into the roaster and sinter feeds is of value.

Lead smelters obtain their arsenic from ores and concentrates, as well as from flue dusts shipped from other plants, particularly copper smelters. The percentage of arsenic in ores is usually low, although occasional lots of high arsenical products are smelted. These crude ores may be sulphides, as arsenopyrite; or oxides like scorodite, which carry gold or lead minerals.

The small amount of arsenic in the original ores received is greatly increased by a circulating load of arsenic in secondary products that are resmelted for their lead or precious metals. More important than the arsenic present directly in the concentrates treated is that in fumes and dusts that may originate in the blast furnace or sinter plant of the lead smelter, or may come from a copper smelter as lead-bearing converter fume or roaster dust. Thus the lead smelter not only must treat its own arsenic but is compelled to handle that from some copper and perhaps other lead plants.

Where copper and lead plants exchange products, each plant may be forced to re-treat part of the arsenic it has shipped outside its own confines. Speiss from the lead blast furnace contains chiefly iron and arsenic with some lead, copper and sulphur and often appreciable amounts of gold and silver. If its copper content is sufficient this speiss may be sent to the copper smelter where usually it is treated in the converter and the copper is separated as blister. Much of the arsenic and most of the lead are recovered as converter fumes

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and are sent back to the lead plant, with perhaps other arsenical products accumulated from copper ores.

In most lead plants, arsenic is removed incompletely during roasting and sintering. Arsenic that finds its way into the lead blast furnace must be removed as fume, in speiss, or in the bullion, and each of these products must in consequence be re-treated. Therefore, removal of the arsenic before the charge is sent to the blast furnace is desirable. The best point of exit seems to be during roasting at the lead plant, because arsenic so removed can be condensed, purified and prepared for sale, and thereby removed definitely from the smelting circuit. This roasting is accomplished in some lead plants by the use of Godfrey single-hearth roasters. In other plants multiple-hearth roasters such as the Wedge are employed.

The gases leaving the tops of lead blast furnaces at some plants are strongly reducing. Arsenical compounds may then be reduced in the upper part of the smelting column. Iron is supposed to aid in this reduction. However, the arsenic that is not reduced and volatilized in the upper part of the furnace sinks deeper, and under still more strongly reducing conditions forms speiss or arsenides.

SPEISS

With all possible efforts made to remove arsenic from the blast-furnace charge, it is found in most plants that there is still sufficient arsenic to produce a speiss. Normally this speiss is tapped through the slag taphole into the first settler from which it is tapped into shallow pans for cooling. When solidified it is removed from the pan to a railroad car and transferred to a coarse-crushing mill.

At some smelters provision has been made to granulate this blast-furnace speiss. The advantage of such a procedure is the elimination of coarse crushing; a disadvantage is a lower lead to copper ratio

in the speiss. When tapped this speiss contains some metallic lead, which will be granulated along with the speiss, but when allowed to cool will settle free from the speiss.

The crushed speiss that has passed through a $\frac{1}{4}$ -in. screen is now fed to a dry ball mill. A typical screen test of this feed is as follows: plus 8-mesh, 25 per cent; minus 8, plus 14-mesh, 65; minus 14-mesh, 10.

A satisfactory ball mill for this service has a diameter of 8 ft. 10 in. and a length of 4 ft. The ground speiss is generally passed through a 10-mesh screen. A typical screen test of this product is as follows:

	PER CENT
—10+14-mesh.....	4.75
—14+28-mesh.....	23.78
—28+48-mesh.....	22.35
—48+100-mesh.....	18.05
—100-mesh.....	31.07
Total.....	100.00

Another disadvantage of granulating the speiss is that the moisture contained in this material causes clogging of the ball-mill screens because of the steam created. This difficulty, which greatly reduces the tonnage, may be partly overcome by mixing granulated speiss with crushed speiss.

Satisfactory roasting of speiss has been obtained when mixed with baghouse dust, Cottrell dust, arsenical dust, or other arsenic-bearing material, along with the proper amount of sulphide diluent. Also, speiss may be satisfactorily roasted by mixing only with sulphide diluent.

It should be noted that experience indicates that each material seems to have an optimum roasting temperature, draft requirement, and charge mixture for greatest speed in removing arsenic. It is desirable, therefore, to keep each arsenic-bearing material more or less by itself in the arsenic-roasting process. In other words, with different roasting charac-

teristics, better results can be obtained if each material is roasted by itself. Experience has taught us that a temperature of 1300°F . and draft of 0.02 to 0.04 in. of water gives the most satisfactory speiss-roasting results. A mixture of 60 per cent sulphide diluent and 40 per cent speiss has been found most satisfactory. Tonnage through a 26-ft. Godfrey roaster varies from 35 to 50 tons of total charge per 24 hr. In most arsenic roasting of the speiss the calcines can be reduced to about 2 per cent arsenic or less.

The treatment of the calcines or residue from arsenic roasting of the speiss will be determined by the metal content of the calcines. If the percentage of copper is high, and if the copper to lead ratio is reasonably high, say 3:1, the calcines should be treated through the copper smelter. If the percentage of copper is low and the copper to lead ratio is low, probably the calcines will be treated best at the lead plant. If the latter proves more economical, the calcines are incorporated in the Dwight-Lloyd charge, sintered and smelted through the blast furnace.

COPPER COLLECTORS—MATTE AND SPEISS

Lead metallurgists have given the subject of lead drosses a great deal of attention for many years, but only recently has the problem of economical treatment approached satisfactory solution. For many years it was customary for lead smelters to produce matte in their blast furnaces, as this was the form in which copper could be collected, concentrated if necessary, and shipped to the copper smelters for further treatment.

The main prerequisites for good matte formation, of course, are a more or less definite amount of copper on the charge and sufficient sulphur. Impurities such as arsenic and antimony, which prove troublesome, have been ignored as far as possible

even though they contaminated the bullion and therefore increased refinery costs.

During the early years part of the copper in the blast furnace went to dross, which was fed back to the furnaces currently, with the result that arsenic and antimony tended to build up until the arsenic could effect a combination with the copper and iron and an alliance with lead, and the antimony a combination with copper and an alliance with lead. Sulphur, being the most active agent in taking up the copper, left little of that element for the arsenic and antimony, so that on the whole a somewhat unsatisfactory metallurgy resulted.

The substitution of the dross reverberatory for the blast furnace for smelting dross in 1927 eliminated the necessity for any considerable amount of slag formation, always associated with blast-furnace practice. In the reverberatory operation it is advantageous to produce a fluid slag relatively free from entrained metals, particularly copper, but the composition need not adhere to close fluxing limitations for successful operation. As the slag from the dross reverberatory ordinarily was re-treated either in a lead blast furnace or in a copper reverberatory, it was considered good practice to produce as little slag as was consistent with sufficient fluidity. No attempt was made to regulate the fluxing to assure a high copper to lead ratio in the matte tapped from the dross charge. Quite satisfactory results were obtained in this manner, but the process had the disadvantages of the extra handling and increased fuel.

A little later a similar operation was practiced whereby arsenic, rather than sulphur, was the principal collecting medium for the copper, producing a speiss of fair copper to lead ratio.

This change from matte to speiss production brought about an improved copper to lead ratio with slag conditions unchanged. The formation of speiss was stimulated later by the addition of more

arsenic through the introduction of liquid blast-furnace speiss to the reverberatory. This practice produced a low-copper speiss but carried a higher copper to lead ratio than had been obtained previously. Such a procedure had the disadvantage of shipping a low-copper concentrated product, which necessarily increased the freight per pound of copper and at times removed from the plant iron that required replacement.

DROSS

The important constituent of copper-lead dross that makes it refractory to smelt by the practice mentioned is magnetic oxide of iron, this generally being present in amounts varying from 2 to 5 per cent. In the so-called standard process, the iron is removed as a silicate slag by adding siliceous ores and scrap iron and operating at a temperature between 2400° and 2600°F . This means high fuel consumption and slag high in lead and copper, which has to be re-treated in the lead blast furnace, and a lead bullion from reverberatory running to 2.5 per cent copper. The two latter features cause a large circulating load of copper, making increased tonnage of copper-lead dross to be resmelted.

Most important of all, this method yields a copper shipping product with a low copper to lead ratio; that is, the analysis of shipping speiss runs from 40 per cent copper and 20 per cent lead to 45 per cent copper and 15 per cent lead.

SODA PROCESS

About two years ago, E. P. Fleming and D. H. McIntosh, metallurgists of the research staff of the American Smelting and Refining Co., suggested and worked out a new metallurgy for the treatment of lead drosses in the reverberatory furnace. The main object of this new process, known as the soda process, is to realize a low-temperature smelting operation for the treatment of lead drosses in the re-

verberatory and produce a high-copper speiss with a high copper to lead ratio. Fleming and McIntosh thought that by the use of soda it might be possible to break up the copper antimonide and copper arsenide compounds that were responsible for retention of gold and the occlusion of lead, with the formation of a low-temperature fusible charge. While they found that the arsenide and antimonide compounds were too stable to be affected by the soda, they developed a mixed flux that had a marked effect on the lead-speiss separation. This flux, within certain narrow limits, has the following composition: sodium carbonate, 4.0 per cent by weight of dross; fine coke, 1.5; litharge, 1.5.

Soda ash, which is the most important reagent, will slag off the magnetic oxide of iron and other refractory subjects, such as small amounts of silica, at a working temperature of about 1700°F . The iron is removed partly in chemical combination with soda, partly in solution and partly in suspension in the soda matte. This soda matte contains practically all the iron and sulphur and generally has a good enough copper to lead ratio to allow shipment direct to the copper smelter. A typical analysis of this soda matte is copper 15 per cent, lead 3, iron 16 and sulphur 7. Here the copper to lead ratio is 5:1, and the shipment of this copper materially reduces the circulating load of copper in the lead plant as compared with former standard practice. At times this ratio can be carried to 10 to 1 with conditions satisfactory.

The amount of soda required for proper functioning of the process depends to a great extent upon the amount of iron oxide present. In general, the operating limits are from 3 to 5 per cent by weight of dross. The small amount of coke, varying from 1 to 2 per cent by weight of dross, is necessary for the reduction of the small amount of lead oxide present. The use of litharge and the function it plays is still a little bit

in doubt. In treating some drosses we have been able to dispense with the litharge. Apparently the lead in these drosses had oxidized slightly. On other drosses we find that the addition of a small amount of litharge up to 2 per cent by weight helps to improve the copper to lead ratio.

CYCLE OF OPERATIONS

Although the operating routine varies from plant to plant, owing to handling equipment and local conditions, there is a definite similarity in procedure.

The present method of removing dross from lead bullion is, first, to take crude lead from the blast furnace and transfer it to a drossing kettle of 30 to 65 tons capacity, where it is freed from impurities held in suspension or solution. When sufficient lead has been received into a kettle, a mechanical stirrer dries the dross and mixes in the soda ash that had previously been added to the kettle. The amount of soda varies between 3 and 5 per cent, depending upon the amount of dross and its iron content. The lead dross and soda are continuously stirred until the kettle is filled and the dross is well dried. It is essential that the soda be thoroughly mixed with the dross.

The dross is removed by use of an "Owens" grab bucket attached to a crane or by skimming with a perforated spoon. Before the Owens bucket is moved, with its load of dry dross or the basket, a mixture of one part fine coke and one part litharge is added to the top of the dross. The dross is then charged to the reverberatory. The dross is charged at intervals, but never allowed to pile up—all dross is smelted before new dross is added.

A full furnace will accommodate a metal bath of 30 to 45 in. Tapping of metals is made as required. The soda matte is removed first. It is important that all matte be taken, otherwise magnetite may separate out and cause accretions to form. In general there will be about 2 in. of matte on the

bath, all of which is skimmed off. Then about 3 in. of lead is tapped from below until speiss shows, leaving an appreciable heel of lead in the furnace, which acts as a balance wheel to hold the temperature. The temperature of the lead at the time of removal is about 1120°F. After removal of the lead, the furnace will contain from 21 to 28 in. of speiss. From this amount will be drawn 6 to 9 in. of the upper portion of the speiss, of which the temperature will be about 1300°F. This upper layer is low in lead and high in copper. The layer of speiss directly above the lead contains more lead and less copper. Temperature control is very important in this operation and recording thermometers should be used for this purpose. Proper tapping is necessary in order to secure clean speiss.

Operating at 1700° to 1900°F., there is a material saving in fuel and a saving on the wear and tear of brickwork. Water cooling of the furnace on the soda line has been found advantageous. The lead bullion obtained from the dross reverberatory contains only 0.5 per cent copper, as compared with 2 to 3 per cent copper under standard practice. This also has a very important effect on reducing the circulating load of copper. Most important, however, is the grade of shipping copper speiss produced. Instead of running 45 per cent copper and 18 per cent lead, or a ratio of 2.5:1, the speiss from the soda treatment generally runs to 60 per cent copper and 8 to 10 per cent lead. The conditions responsible for this high copper ratio can generally be attributed to low-temperature operation, which permits low solubility of lead in speiss and the liquation from speiss of all metallic lead.

The presence of the impurities now removed by soda was previously responsible for a surface-tension phenomenon that caused the speiss to occlude the metallic lead. Magnetite, etc., can be removed by soda at a lower temperature than where silica and scrap iron are employed as fluxes.

At lower temperatures the solubility of lead in copper arsenide and copper antimonide is naturally reduced. The compound copper arsenide accounts for approximately 75 per cent of speiss composition. At the freezing point of this compound, which is approximately 1225°F. , it will contain about 6 per cent lead in solution. At 1900°F. , it will contain approximately 16 per cent lead in solution. The furnace can operate in a satisfactory manner with speiss at a temperature of 1500° to 1700°F. , which will carry from 9 to 11 per cent lead. It is advantageous, therefore, to operate at a low temperature. The production of a silicate slag does not permit low-temperature operation.

Chemical and microscopic examination of the speiss produced indicates that we are nearing a true mixture of copper

arsenide and copper antimonide with a minimum of lead in solution and scarcely any in suspension. Nothing except cupellation of lead can be done in the dross reverberatory to affect the copper arsenide and copper antimonide compounds.

We believe the soda process for handling lead-plant drosses has shown more possibilities of good metallurgy and sound economical operation than any process thus far used.

ACKNOWLEDGMENTS

The author takes this opportunity of acknowledging the assistance of Messrs. R. A. Wagstaff, E. P. Fleming, and A. A. Collins, of the American Smelting and Refining Co., in the preparation of this paper and thanks are due to members of the technical staff of the Murray plant.

Some Experiments on Sintering Lead Sulphate Products

By G. L. OLDRIGHT* AND S. F. RAVITZ,† MEMBERS, AND HENRY DE RYCKER,‡ JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1940)

THE upper limit of richness of concentrates that can be smelted by means of the blast furnace without added diluents is fixed by the operation of sintering. A sinter feed with normal gangue constituents, containing more than about 50 per cent of lead, tends to fuse; as a result, air does not come sufficiently into contact with the sulphides at roasting temperatures, and sulphur elimination is poor. Since most lead concentrates now contain 55 to 80 per cent lead, it is necessary to add diluents to lower the grade of such sinter feed to about 50 per cent or less. This not only entails the expense of providing barren diluents when adequate diluents containing precious metals are not available but also appreciably lowers the capacity of the blast furnace to produce lead and increases slag losses.

Attempts to desulphurize rich lead concentrates by methods other than sintering have not proved successful. Flash roasting, for example, converts much of the lead sulphide to lead sulphate rather than to oxide. However, this suggested the possibility that deliberate flash roasting of the concentrates to sulphate, followed by sinter roasting of the resulting product, might prove promising, particularly inasmuch as the elimination of sulphur from lead sulphate requires heat alone and not contact with atmospheric oxygen.

The sintering of lead sulphate products has additional interest because important amounts of such products are now treated by lead smelters. Considerable quantities of lead sulphate are present in rich lead flue dusts and other by-products; lead-chamber sulphuric acid plants and other

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chemical plants also make available a considerable tonnage of high-grade lead sulphate resulting from the corrosion of lead equipment.

The only reference found on sintering rich lead sulphate products was a statement by H. J. Stehli¹ that "lead sulphate acid sludge" had been successfully sintered with carbon to make cakes containing up to 80 per cent lead and less than 1 per cent sulphur. (No further details were given.)

In this investigation, laboratory experiments were made on the sintering of lead sulphate products from three different sources: (1) flash-roaster residue from an ignition and settling chamber used in flash-roasting very high-grade galena concentrates; (2) flash-roasted lead sulphate, a high-grade fume used commercially as a pigment; and (3) high-grade lead sulphate sludge from a lead-chamber sulphuric acid plant. The large amount of work that has been done on pigments has shown that the physical differences between precipitates and the fumes are marked. Sublimed lead sulphate does not show well-defined crystals and has remarkable uniformity of grain; in contrast, precipitated lead sulphate is relatively coarse and crystalline.²

EQUIPMENT AND PROCEDURE

Most of the sintering tests were made in a small, downdraft, stationary-hearth, sintering pot, which consisted of a piece of 4-in. pipe about 7 in. deep, at the bottom of which was a grate made of a $\frac{1}{2}$ -in. cast-iron disk through which holes were drilled at $\frac{3}{8}$ -in. centers. These holes were $\frac{1}{8}$ in. in diameter at the top and about $\frac{1}{4}$ in. at the bottom, to minimize plugging. The draft was supplied by a small Roots blower and was controlled by a by-pass valve through which air could enter the suction of the blower directly, thereby lessening the air flow through the sinter column. The draft was measured by means of a manometer entering the system just below the sintering pot. To enable the flow of air through the sinter column to be kept uniform from test to test, a plate-orifice flowmeter was inserted between the pot and the by-pass valve. The initial height of the sinter column was always 4 inches.

The charge was ignited by a burner that consisted of a 1-in. pipe manifold, at right angles to which were connected a number of capped $\frac{1}{4}$ -in. pipes spaced about 1 in. apart in the clear. The gas-air mixture for ignition passed through $\frac{1}{16}$ -in. holes spaced about $\frac{3}{4}$ in. apart on the underside of the $\frac{1}{4}$ -in. branch pipes. The flames covered the entire area of the sintering pot and overlapped all sides; for uniform ignition, it was found best to leave a few inches vacant in the pot above the sinter column.

Confirmatory tests were made with an 8-in. pot. In general, the charge was easier to ignite uniformly, and the results were better with the

¹ *Trans. A.I.M.E.* (1936) **121**, 42.

² M. Toch: *Chemistry and Technology of Paints*, 31 et seq. New York 1925. Van Nostrand.

larger pot. To conserve materials, however, the 4-in. pot was used for most of the tests.

The factors governing ignition, fusion, porosity, desulphurization, and sintering in general are qualitatively the same in the small test pots as with commercial machines. Experience has shown that small-scale experiments on sintering indicate the conditions that will be successful in plant practice.

Preparation of the charge was found to be exceedingly important. In almost all the tests coke was added as fuel, and water was included to give the desired physical properties. It was necessary to exercise the greatest care to obtain an intimate admixture of the lead sulphate, coke and water. After considerable experimentation, the following procedure was adopted as standard, and unless specified otherwise was used in all the tests.

Any lumps or large particles were broken by crushing the lead sulphate product to minus 20-mesh. It was then mixed thoroughly by hand with minus 65-mesh coke until the mixture was of uniform color (coarser coke, for example -10+20-mesh, gave a crumbly sinter cake). The material was mixed further by forcing it through a 20-mesh sieve with a wire brush. (Incidentally, passing material through a sieve is one of the best methods of mixing—for reasons of cost the sieve should be as coarse as will give the requisite intimacy of mixture, particularly if the material is moist.)

It was difficult to mix the water and the solid constituents intimately enough to avoid the formation of hot and cold spots in the charge during sintering. It was necessary to add the water in small successive batches, each of which was mixed by hand with the mixture of lead sulphate and coke, care being taken to break up any lumps formed. Final mixing was effected by passing the material through an 8-mesh sieve.

In many of the tests previously sintered material, first crushed to minus 20-mesh, was included in the charge.

Before the moistened charge was bedded in the sinter pot, some finely divided (minus 20-mesh) feed was sieved out, the remaining material was remixed and placed in the pot, and the finely divided material was sprinkled on top of the charge. This procedure aided materially in obtaining prompt and uniform ignition. The compactness of the bed before ignition was an important factor. By bedding the charge in such a manner that the draft and the air flow through the bed were the same for a given series of tests it was possible to make the tests under comparable conditions and to duplicate tests satisfactorily.

Sampling the sinter cake was a difficult problem. Usually the top quarter inch or so and a thin layer along the sides were poorly sintered; at times the bottom was contaminated with unburned material and often contained much metallic lead. These portions were cut away, and the sample, in most instances, was taken from the remaining material, any

coarse metallic lead being rejected. In consequence, the results reported are conservative, being lower in lead and higher in sulphur than they would have been if thoroughly representative samples of the sintered material, including all the metallic lead, had been obtained.

SINTERING OF FLASH-ROASTER RESIDUE

The first lead sulphate product used in these experiments was obtained, as explained, from an ignition and settling chamber used in flash-roasting very high-grade galena concentrates. Compared with fume, the particles were relatively granular, nodules as large as $\frac{1}{4}$ in. being present. The analysis and calculated composition of the material are given in Table 1.

TABLE 1.—*Composition of Flash-roaster Residue*

Analysis, Per Cent		Calculated Composition, Per Cent	
Total sulphur.....	6.4	Lead sulphide.....	19.4
Sulphide sulphur.....	2.6	Lead sulphate.....	36.0
Sulphate sulphur.....	3.8	Lead oxide.....	41.9
Lead.....	80.3	Impurities (by difference).....	2.7
			100.0

Since the total sulphur content was only 6.4 per cent, approximately that of the usual feed to the final sintering machines in practice, it was first attempted to sinter this product in a single pass. The results of a few typical tests are shown in Table 2.

TABLE 2.—*Sintering Flash-roaster Residue with Carbonaceous Fuel*

Experiment No.	Size of Feed, Mesh	Added, Per Cent		Sulphur in Cake, Per Cent	Remarks
		Water	Coke		
9	—4	3	2	4.45	No special preparation or bedding of feed. Cake porous and hard.
11	—20	3	2	4.35	Poor ignition. Sintering incomplete. Center of cake fairly good
18	—20	5 per cent of mixture of 1:1 water and molasses		5.14	Cake fairly good
Special..	0	0	2.44	Material fused by heating in crucible

Preliminary tests with as much as 5 per cent coke showed that if much coke were used there was considerable metallic lead on the grate, the flow of air was partly obstructed, the cake fused, and very little sulphur was eliminated.

Test 18 was one of several in which waste sugar-beet molasses was added as fuel to distribute the heat as uniformly as possible. The use of molasses gave a cake of good physical properties, but did not remove much sulphur.

The special test, in which the charge was fused, was made to determine the effect of temperature alone on the removal of sulphur: 2.44 per cent sulphur remained. Apparently little sulphur was removed from the lead sulphide, notwithstanding the large excess of oxidized lead compounds.

Tests were next made to determine the effect of lead sulphide as fuel. The results of a typical series of tests are given in Table 3.

TABLE 3.—*Sintering Flash-roaster Residue with PbS as Fuel*

Experiment No.	Feed	Added, Per Cent		Sulphur, Per Cent		Physical Nature of Cake
		Water	PbS	In Charge ^a	In Cake	
201	Fresh	5	29	8.4	9.45	Many large, unburned nodules
202	Sinter 201 crushed	0	0	9.45	6.95	Poor ignition. Lower half of cake fairly good
203	Sinter 202 crushed	2.25	29	8.8	6.85	Poor

^a Exclusive of water.

The use of galena as fuel, to avoid the use of coke, was not promising; too much galena was required, little sulphur was removed, and the resulting semifused cake was poor.

Finally some experiments on double-sintering the flash-roaster residue were tried, using coke as fuel. The tests were unsuccessful. When the final charge was ignited with a strongly oxidizing flame the top of the charge fused and the rest of the cake was desulphurized but little. It was concluded that there was little chance of desulphurizing satisfactorily a rich lead product, even if partly oxidized, when much of the sulphur occurred as lead sulphide.

SINTERING OF FLASH-ROASTED LEAD SULPHATE PIGMENT

The relatively coarse lead sulphide particles that settled in the heating chamber of the flash roaster were, in all probability, coated with oxides, which insulated the kernels of lead sulphide from the air. The next product tried was a lead sulphate pigment formed by the sulphation of galena particles burned in suspension; the pigment particles had no unaltered lead sulphide kernels. The composition of this product is given in Table 4.

TABLE 4.—*Composition of Flash-roasted Lead Sulphate Pigment*

Analysis, Per Cent		Calculated Composition, Per Cent	
Total sulphur.....	9.06	Lead sulphide.....	None
Sulphate sulphur.....	9.06	Lead sulphate.....	85.7
Sulphide sulphur.....	None	Lead oxide.....	13.4
Lead.....	71.0		—
Insoluble.....	None	Total.....	99.1

Sintering the flash-roasted lead sulphate in a single pass was attempted first. It was found that about 14 per cent of water was needed to provide the proper porous structure of the feed as bedded in the sinter pot. With such a large amount of water, much coke was needed to supply heat and little sulphur dioxide was evolved. (The large amount of moisture that a freshly cottrellled fume, for instance, will "take" without becoming a mud is often taken advantage of in making sinter at lead smelters when it is desired to add more moisture to the charge.)

It was found, however, that previously sintered material could be mixed with fresh lead sulphate pigment to give a feed requiring much less water to provide the requisite porosity and other properties for good sintering. By using a mixture of fresh lead sulphate and preroasted sinter, cakes of good physical properties with reasonably low sulphur content could be obtained. The ratios of lead to sulphur in the final cakes were as high as those usually obtained in good sintering-plant practice.

TABLE 5.—*Sintering Flash-roasted Lead Sulphate*

Experiment No.	Charge	Added, Per Cent		Analysis, Cake, Per Cent		Ratio, Lead to Sulphur	Remarks
		Coke	Moisture	Sulphur	Lead		
A1	½ fresh feed	2	5	4.0	82.0	20.5	Good cake
A2	½ crushed preroast ½ fresh feed	2	5	3.05	85.45	28.0	Best sinter analysis obtained
	½ crushed sinter A1 ^a						Good cake
B1	Similar to A1	2	5	3.49	83.80	24.0	Good cake
B2	Crushed sinter B1	0	5				Like cake B1
B3	Crushed sinter B2	0	5	3.51	83.60	23.9	Exceptionally good cake
							Cokelike structure
C1	Similar to A1	2	5	3.51	85.10	24.3	Test made in 8-in. pot. Good cake

^a Crushed to minus 8-mesh; sieved on 10-mesh sieve; oversize used.

Table 5 gives the results of some tests in which the original charges consisted of half fresh lead sulphate and half preroasted material made up of the cakes from various unsuccessful preliminary experiments.

These and similar tests proved that sinters of good physical properties and satisfactory chemical composition could be obtained by a process of return-sintering. The amount of coke used, however, had an appreciable effect on the nature of the final cake obtained and therefore was investigated more carefully. A series of tests was made, using one part of fresh lead sulphate to two parts of "preroast." The "preroast" consisted of sinters from various earlier tests, crushed to minus 65-mesh and thoroughly mixed; this composite "preroast" contained 80.4 per cent lead and 3.22 sulphur. Varying amounts of coke and 6 per cent water were used in preparing the charge. To obtain comparable analyses, the entire sinter cakes were sampled. The results of the tests are given in Table 6.

TABLE 6.—*Effect of Coke on Sintering of Flash-roasted Lead Sulphate Pigment*

Charge: $\frac{1}{3}$ lead sulphate pigment (71.0 per cent Pb, 9.06 per cent S)
 $\frac{2}{3}$ preroast (80.4 per cent Pb, 3.22 per cent S)

Analysis of charge, exclusive of moisture and coke: 77.3 per cent Pb, 5.17 per cent S. Water added, 6 per cent.

Experi- ment No.	Coke in Feed, Per Cent	Analysis of Cake, Per Cent				Per Cent Total Sulphur as Sulphide	Ratio Lead to Sulphur in Cake
		Lead	Total Sulphur	Sulphate Sulphur	Sulphide Sulphur		
1	2.0	80.42	3.49	3.25	0.24	6.9	23.0
2	2.5	81.97	3.52	3.25	0.27	7.7	23.3
3	3.0	82.17	3.35	2.90	0.45	13.4	24.5
4	3.5	83.61	3.13	2.48	0.65	20.8	26.7

SINTER CAKES MADE IN GOOD COMMERCIAL PRACTICE

		51.4	2.4				21.4
		45.0	1.7				26.4
		38.0*	1.6*				23.8

* Recent monthly average in a large Western smelter.

As the percentage of coke increased, the total amount of sulphur decreased, while the amount present as sulphide increased. If the percentages of total and of sulphide sulphur are plotted against the percentage of coke added and the resultant curves extrapolated, it can be estimated very roughly that if 5 per cent of coke was added all the sulphur would be present as sulphide and the sulphur content would be about 2.4 per cent.

Progressive hardening of the sinter cakes as the coke added was increased from 2.0 to 3.5 per cent is brought out in Fig. 1, which shows the four cakes cut in two vertically. It is surprising that such a high-grade

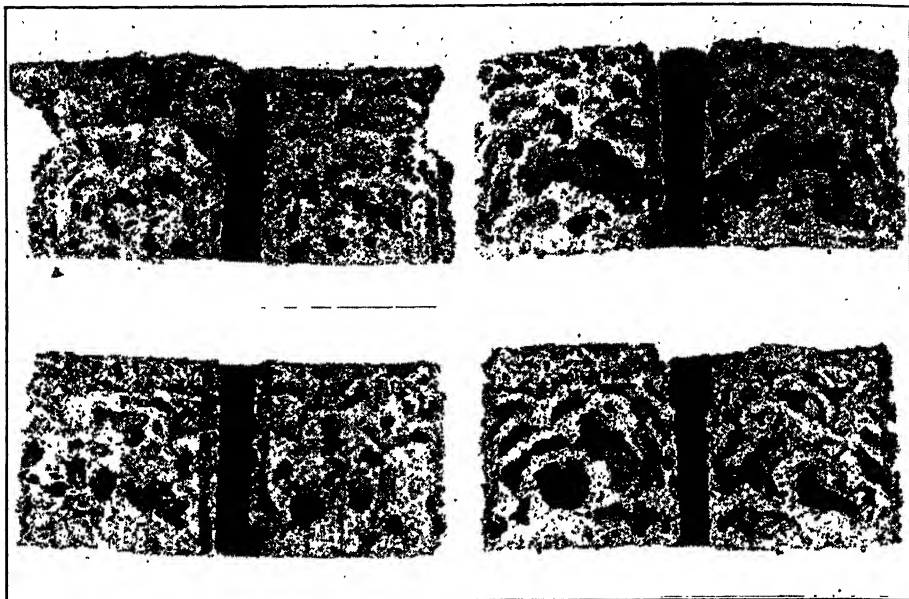


FIG. 1.—VERTICAL SECTIONS THROUGH SINTER CAKES.

Showing structure of cakes and increasing hardness with increasing amounts of coke.

a, 2 per cent coke.

b, 2.5 per cent coke.

c, 3.0 per cent coke.

d, 3.5 per cent coke.

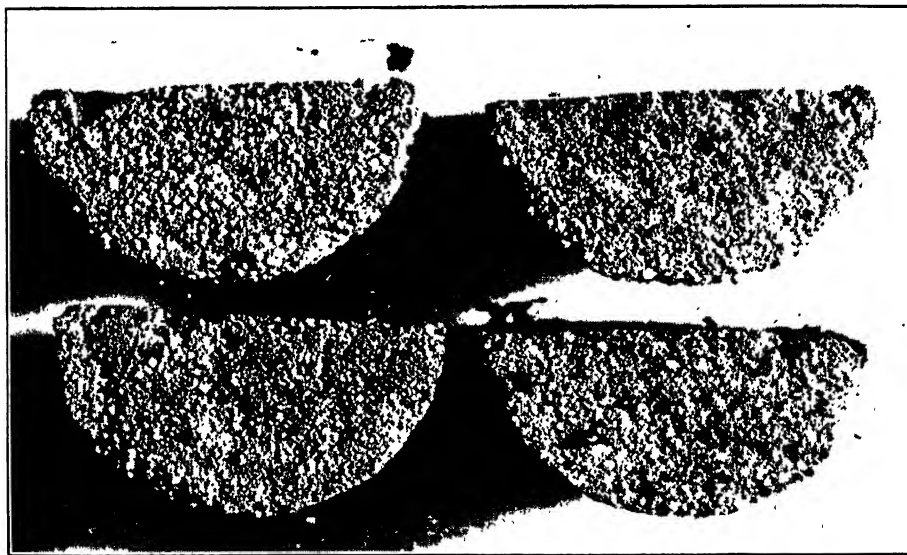


FIG. 2.—BOTTOMS OF SINTER CAKES.

Showing increasing amounts of metallic lead with increasing amounts of coke.

a, 2.0 per cent coke.

b, 2.5 per cent coke.

c, 3.0 per cent coke.

d, 3.5 per cent coke.

lead product, containing as fluxing ingredients only the 10 per cent of ash in the coke, should form such a hard sinter. That the presence of metallic lead should be no more pronounced was likewise unexpected. There was, however, considerable metallic lead in the bottoms of the cakes. Fig. 2 shows these bottoms photographed with the light falling from the right to bring out the shadows thrown by the lead projections formed by the molten metal that had run down into the holes in the grate. The increase in metallic lead as the percentage of coke in the charge was increased is also shown clearly.

SINTERING OF LEAD-CHAMBER SLUDGE

As noted, considerable tonnage of lead sulphate is available near industrial centers as sludges formed from the corrosion of lead in chemical plants; e.g., in lead chambers for making sulphuric acid. After the free sulphuric acid has been washed out, the material may be fairly pure.

It was felt that comparison of the behavior of such material with that of flash-roasted lead sulphate pigment would be of interest. Accordingly, some sludge was obtained from the chamber sulphuric acid plant at Garfield, Utah. After being washed, this sludge analyzed as shown in Table 7, in which the composition is compared with that of pure lead

TABLE 7.—*Composition of Lead-chamber Sludge and of Pure Lead Sulphate*

Constituent	Analyses, Per Cent	
	Sludge	Pure PbSO ₄
Lead.....	67.6	68.3
Sulphide sulphur.....	0.1	
Sulphate sulphur.....	10.55	10.6
Oxygen with sulphate.....	21.1	21.1
	99.35	100.0

sulphate. The material then was virtually pure lead sulphate; apparently it contained very small amounts of sulphide dust and of free sulphuric acid that had not been completely washed out.

After being washed, dried, and crushed, the sludge was mixed carefully with coke and water as described earlier. It was found possible to obtain good sinter cakes in a single roasting operation, as shown by the typical results in Table 8.

The effect of the amount of water added to the charge was very interesting. It was determined experimentally that 6 per cent water gave the charge the maximum volume per unit of weight; that is, the greatest porosity. Yet tests made with this amount of water resulted in sinter cakes containing islands of sintered matter surrounded by

unroasted material, and relatively poor sulphur elimination. With 10 per cent moisture the cakes were much more homogeneous, although the charge as bedded was definitely wet.

TABLE 8.—*Sintering Lead-chamber Sludge*

Experiment No.	Coke Added, Per Cent	Water Added, Per Cent	Analysis of Cake, Per Cent			Ratio Lead to Sulphur	Nature of Cake
			Lead	Total Sulphur	Sulphate Sulphur		
G-18	—65 mesh, 4 —10+20 mesh, 2	10	82.5	3.50	0.50	23.6	Good, but rather crumbly
G-19	—65 mesh, 7	10	83.89	3.35	0.46	25.1	Good
G-20	—65 mesh, 10	10	84*	2.89		29*	Good

* Estimated; determination lost.

SUMMARY

Rich lead sulphate products containing little or no sulphur as sulphide have been sintered on a laboratory scale to cakes having good physical properties and lead-to-sulphur ratios at least as high as those obtained in good lead-smelter sintering practice. For example, cakes containing about 83 per cent lead and 3 per cent sulphur have been made from a flash-roasted pigment consisting of 86 per cent lead sulphate and 13 per cent lead oxide, and from a sulphuric acid lead-chamber sludge that was almost pure lead sulphate. The sludge was sintered satisfactorily in a single roasting operation, but the flash-roasted pigment required a return-sinter process. Proper proportioning of coke and of water, great intimacy of admixture of all the ingredients, and careful bedding of the charge were essential for successful sintering.

Attempts to sinter without dilution a rich product containing 19 per cent lead sulphide, 36 per cent lead sulphate, and 42 per cent lead oxide were unsuccessful.

The investigation indicated that there is little chance of satisfactorily sintering rich lead products containing appreciable amounts of lead sulphide.

DISCUSSION

H. J. STEHLI.*—It is possible to sinter charges of galena much higher in lead than 50 per cent, but this must be done with an amount of care much greater than is usually given in most lead-sintering plants, particularly with reference to the mixing of the charge. In

most lead-sintering plants this is a very sketchy performance, because of the type of mixing apparatus used.

Charges high in lead sinter much more slowly, for one thing, and a charge having 75 per cent lead would take at least double the time to sinter that a charge with 50 per cent would.

One of the principal reasons high-lead charges cannot be treated without dilution is not so

*Sintering Machinery Corporation, New York, N. Y.

much any limitations of the sintering as limitations due to zinc contents of the concentrates, for instance. A concentrate carrying 75 per cent lead and 3 per cent zinc, if sintered and smelted without admixture of other material, would make an insufficient amount of slag to carry off the zinc. A concentrate with 75 per cent lead will have a minimum of 12.2 per cent sulphur, and if it has 3 per cent of zinc, the probabilities are that the sulphur will be at least 13 per cent. This adds up to 91, leaving only 9 per cent for the material to form the slag. A slag composed of 9 parts of slag-forming material and 3 parts of metallic zinc would be absolutely impossible—no furnace could be kept running on a charge of that sort. I think we are safe in saying that in most cases the zinc contents of concentrates would make necessary their dilution with other slag-making materials.

The quantities of lead sulphate products—such as acid-plant sulphate sludge, sulphate flue dust from dust collectors, Cottrell precipitators, etc.—are comparatively small, and nowhere that I know of is there a sufficient amount of such material produced to make it desirable to run it alone.

I know of no place where such lead sulphate charges are sintered by themselves. They are almost invariably mixed with other lead-bearing products for the furnace charge.

The principal commercial source of lead sulphate has not been mentioned in the paper; that is, scrap from wornout storage batteries.

The filler in the grids of the battery plate—which originally is lead oxide—has been largely converted to lead sulphate in the wornout batteries; also, the sludge accumulating in the bottoms of the batteries is largely lead sulphate. The old battery plates usually are sweated to melt out the antimonial lead of the grid, and the material remaining is a mixture of metallic antimonial lead, lead sulphate, lead oxide and miscellaneous dirt and rubbish.

This particular sulphate material is sintered alone, unmixed with other material, at some of the plants treating lead secondaries.

The authors do not give the vacuum used in their sintering experiments, so I have no way of telling whether that may have been partly responsible for the unsatisfactory results.

The sintering pot used is entirely too small, I believe, to accomplish satisfactory results.

A 4-in. pot has a perimeter of about 12 in., and a cross section of about 12 sq. in., so that there is 1 sq. in. of metal container surface to radiate and conduct away heat for each cubic inch of charge. In the smallest commercial sintering machines, there is 1 sq. in. of such radiation surface to each 20 cu. in. of charge. A 4-in. pot, therefore, has 20 times as much loss from radiation and conduction as a commercial machine.

Take this, in connection with the fact that in most cases the amounts of fuel used by these authors were materially less than required on a commercial machine for a similar charge, and it is very evident there was a great deficiency in fuel.

It is possible to sinter materials that are easily sinterable in a pot of 4-in. diameter, but materials at all difficult to sinter would not produce any results at all in a pot of that size. My own experience is that one foot square is about the minimum size of sintering pan from which data of any degree of reliability can be obtained—and even from that size of pan, such things as fuel consumption cannot be determined very accurately.

The 65-mesh coke used in the experiments described would in most cases be much too fine for satisfactory sintering. This is especially true with a material like fume, lead sulphates precipitates, or similar very fine materials, which become sticky when moist. Such materials will completely coat the coke particles on the outside, and insulate it in such a manner that it cannot burn readily—and even if it does burn, the fuel particles are so small that there is insufficient mass action and concentration of heat.

The $-10+20$ coke, which the authors refer to as giving a crumbly sinter cake, would be the size I would invariably use with a material of this sort.

Another thing mentioned is the difficulty of adding the water to the charges. A satisfactory sintering mixture is almost impossible to make by hand with materials of this sort—it must be rolled, to form pellets, and only in this way can the moisture be satisfactorily distributed through the materials.

As a rule, in sintering materials of this sort, large quantities of metallic lead are produced. Ordinarily this amounts to 10 per cent, and sometimes as much as 20 per cent of the

lead contained in the charge. This lead runs through the sinter cake and is found in the air box under the pan. If such metallic lead is not produced, it is generally evidence of improper or incomplete sintering, and, incidentally, the sinter produced from materials of this character does not bear very much resemblance to ordinary sinter made from lead ores. It may consist of a rather fragile product, or it may consist of a material that looks more like metallic crusts than sinter and consists largely of metallic lead.

In the test shown in Table 2, the amount of coke (2 per cent) was absolutely insufficient to produce results. The charge contained only 2.6 per cent *sulphide* sulphur, as against 3.8 per cent *sulphate* sulphur. As the decomposition of sulphate sulphur is an endothermic reaction, the 2 per cent of coke was entirely insufficient to furnish the heat for both reduction and sintering.

It is nearly always necessary to return to the charge an appreciable amount of fine sinter when sintering these excessively fine materials.

The large amount of moisture that fresh fume will take is mentioned. It is exceedingly difficult to sinter fresh fume because of this fact. It absorbs the water and hydrates with the evolution of heat. Fume of this sort must be wet down, allowed to stand several hours before it is used. After hydration is complete, it will still take up a considerable percentage of mechanically held moisture, which will make it possible to make a good mixture.

In all the tests described, the percentage of coke added is much too low to give satisfactory results.

The authors say: "It is surprising that such a high-grade lead product containing as fluxing ingredients only the 10 per cent of ash in the coke should form such a hard sinter." Fluxing or slag-making ingredients are not by any means always necessary to make a sinter; for instance, an exceedingly hard sinter is made from some very high-grade magnetite concentrates, which are almost pure magnetic oxide containing practically no silica, without the addition of anything. Quite hard sinter is made from some zinc concentrates that are almost pure zinc sulphide. An exceedingly hard sinter is made from cement copper or from fine copper shot. The sinter structure is made up entirely of fused copper oxide.

Only in the sintering experiment G-20 on lead chamber sludge did the authors, in my opinion, approach the right coke percentage for making good sinter.

As far as the sulphur content of the sinters is concerned: there would be absolutely no object in reducing these sulphurs below the ratio of, say, 3 per cent sulphur to 83 per cent lead, because the only object of eliminating the sulphur is to avoid making matte in the blast furnace. Sinter charges commonly used on the blast furnaces contain 50 per cent lead and 2 to 2.5 per cent sulphur, and form no matte. Therefore it would be a waste of time and money to try to make sinters having a lower proportion of sulphur to lead than this.

G. L. OLDRIGHT, S. F. RAVITZ and H. DE RYCKER (authors' reply).—In their rough draft, the authors had included a paragraph on present plant and experimental methods for the removal of sulphur from lead products, and subsequent methods of producing lead from these products, as a function of their percentage content of lead. This somewhat extraneous paragraph was deleted and the paper confined largely to the experimental data; these show that by careful preparation of the sinter charge, practically pure lead sulphate, or mixtures thereof with pure oxides, may be desulphurized by sintering, but that little of the sulphur is removed from such rich mixtures when present as the sulphides. It is indicated, then, that by improvements in methods of preparation of the sinter charge (which methods Mr. Stehli notes as "sketchy"), there is promise of desulphurizing by sintering galena in products of any grade where the galena has first been oxidized, if only in part, to the more readily producible lead sulphate. When richer lead-bearing materials can be desulphurized in present plant sintering practice, there will be added incentive to grade up concentrates by removing zinc, or even less harmful impurities. Opportunities will also be added to learn the upper limits of the lead contents of charges that may be most profitably smelted in lead blast furnaces, and the feasibility of first removing part of the lead in other operations.

The rich lead charges were sintered more readily in 8-in. than in 4-in. pots; however, the larger the scale of the experimental work, of

course the less extrapolation there is to plant practice. The successful use of fine coke is noteworthy—part of the problem of blast-roasting lead sulphate is to have sufficient heat present for thermal decomposition, without having local concentrations of CO high enough to reduce the sulphate to the sulphide. Quite

likely much of the fine coke added in the preroasts was enclosed within the slimy charge used, and the fuel not burned until the material was recrushed and reroasted in the final sintering operation. This behavior may explain in part the small amount of coke used for the final sintering operation.

Sulphur Dioxide in Gases from a Dwight-Lloyd Machine Sintering a Low-sulphur Charge

BY REED W. HYDE,* MEMBER A.I.M.E.

(New York Meeting, February 1942)

SOME information has been published on the sulphur dioxide concentration of gases from Dwight-Lloyd machines sintering lead ores but most of this relates to the customary practice in which the charge is relatively high in lead and is sintered in two passes over the machine. It is thought, therefore, that the following observations on sintering in one pass a low-lead, low-sulphur charge may be of interest.

The data were obtained in sintering lead sulphide flotation concentrates mixed with minus 20-mesh oxide ore, the mixture carrying 16.8 per cent Pb and 5.3 per cent S. No returns were used because of the limited amount of sulphur available as fuel, but the mixture pelletized readily to make a satisfactorily permeable bed on the sintering machine.

As there was a possibility that the SO₂ might be utilized, a series of runs was made to determine the concentration of SO₂ in the gases at different points along the wind box, and the effect on this concentration of changes in the wind-box vacuum. Several runs each were made with vacuums (as measured in inches of water at the wind box) of (1) 2 to 1¾ in., (2) 4 to 3½ in. and (3) 6 to 5½ in. The averages of the determinations from each series are plotted on the graph (Fig. 1). The vertical scale shows the percentage by volume of SO₂ (as determined by the Reich method),

and the horizontal scale shows the time expressed as percentage of the total sintering time. Sintering was considered to be complete when no SO₂ could be detected in the gases. In all cases the depth of bed was 4½ in. and the weight of dry charge per square foot of hearth area was 45.2 lb. Other data are given in the table. The volume of gases corresponding to the several points along the wind box at which SO₂ determinations were made could not be measured, but has been calculated from the SO₂ content and sulphur elimination on the assumption that the volume is uniform throughout the sintering period. This is not strictly true, as with a given vacuum the volume usually will drop slightly toward the middle of the period and increase toward the end. However, this assumption is a reasonable approximation.

Several interesting features are brought out by these data. In general, the published data on SO₂ concentration in sintering under ordinary conditions show a high SO₂ concentration in the early stages followed by a rapid decrease in concentration and with relatively little SO₂ in the gases from the last half or third of the operation. In other words, the greater part of the sulphur elimination is obtained in the first third or half of the period.

In these runs, the 6-in. vacuum, which approximates the usual operating condition, gives a curve that follows this customary pattern. Maximum SO₂ concentration is obtained 2½ min. after

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ignition (corresponding to a point about $3\frac{1}{2}$ ft. along the wind box of a 264-in. sintering machine) and from this peak the curve drops rapidly to 1 per cent SO_2

less at the low vacuum. The degree of sulphur elimination is also lower.

In regard to the observed fact that the sintering time with the 4-in. and the 6-in.

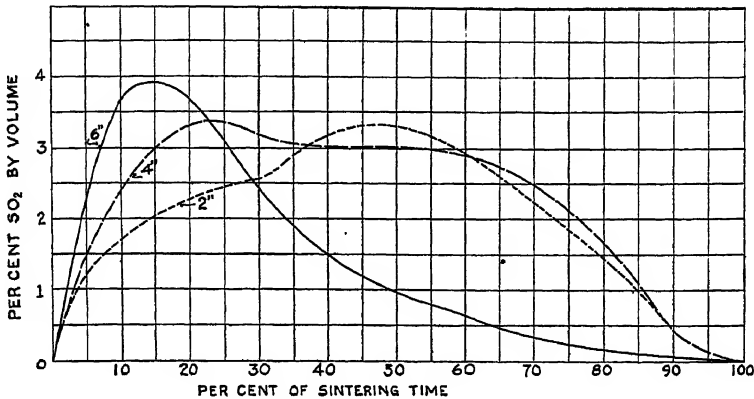


FIG. 1.—AVERAGES OF DETERMINATIONS OF RUNS.

Percentages shown by vertical scale were determined by the Reich method.

at the halfway point (or end of the first wind box).

But with the 4-in. vacuum the peak comes a little later and flattens out to extend over some two thirds of the time period before commencing to fall off rapidly. With 2-in. vacuum the distribution

vacuums was the same, it should be noted that to obtain the information desired from these series of tests the sintering operation was continued until no SO_2 could be detected in the wind-box gases. This differs from ordinary practice, where the cake is generally discharged somewhat

TABLE 1.—Operating Data

$4\frac{1}{2}$ -in. bed; 45.2 lb. dry charge per sq. ft. hearth area; 5.3 per cent S, 16.8 per cent Pb

Wind-box Vacuum, In.	Sintering Time, Min.	Sulphur in Product, Per Cent	Quality	Average SO_2 by Volume in Gases, Per Cent	Average Gas Volume (N.T.P.) per Sq. Ft. Hearth Area, Cu. Ft. per Min.
2-1 $\frac{1}{4}$	24.3	1.29	Friable	2.04	41.4
4-3 $\frac{1}{4}$	17	1.03	Poor	2.29	56.1
6-5 $\frac{1}{4}$	17	0.99	Fair Good	1.35	95.5

is similar to the 4-in. curve, but with the peak at about the mid-point and with no sharp slope on either the rising or falling side.

The time required for sintering this charge was much less at 6-in. vacuum than at 2-in., as would be expected, although the 4-in. and 6-in. vacuums took the same sintering time. It follows that the capacity of the sintering machine is correspondingly

earlier; i.e., while the bottom is still hot and giving off a slight amount of SO_2 . As the curves show, with the 6-in. vacuum a small percentage of SO_2 was found in the gases over an appreciable period beyond what would ordinarily be considered the end point, whereas with the 4-in. vacuum the curve drops more abruptly. No doubt this is due to the markedly greater fusion that took place with the higher vacuum,

which would tend to slow down the oxidation of the sulphur toward the end, as compared with the 4-in. vacuum, where fusion of the charge was much less. From the usual operating standpoint, therefore, the sintering time with the 6-in. vacuum would be less than the 17 min. noted for these tests—probably more nearly 12 minutes.

area, as compared with lower concentration and higher volumes for the lower vacuum operations. At 75 per cent cutoff, the volumes are about the same in all three cases, but gas concentration and quality of sinter cake again favor the 6-in. vacuum. On a sintering machine with two wind boxes, gases from the first wind box at 6-in. vacuum would carry 88 per cent of the

TABLE 2.—*Distribution of Sulphur Dioxide in Wind-box Gases*

Percentage of Total SO ₂	50 Per Cent			65 Per Cent			75 Per Cent		
Distribution	Percentage of Time	Average SO ₂ Concentration	Gas Volume, Cu. Ft.	Percentage of Time	Average SO ₂ Concentration	Gas Volume, Cu. Ft.	Percentage of Time	Average SO ₂ Concentration	Gas Volume, Cu. Ft.
Vacuum, Inches:									
2-1 3/4.....	45	2.25	452	55	2.43	553	62	2.49	625
4-3 1/2.....	42.5	2.72	405	53.5	2.78	510	61.5	2.70	585
6-5 3/8.....	23	2.96	374	30	2.91	488	37	2.76	600

Important from an operating standpoint is the quality of the sinter cake. That made at 6-in. vacuum was hard and strong, excellent blast-furnace feed. At 2-in. vacuum the sinter was markedly friable and of poor quality, showing lack of the heat concentration necessary to effect proper sintering. This was to be expected, since the amount of fuel available in the charge was insufficient to give the necessary temperature when burned over the longer time period. The 4-in. vacuum cake was of intermediate quality, but still not of satisfactory character.

Table 2 has been calculated to show the distribution of the SO₂ in the wind-box gases and indicates that the higher vacuum gives the most favorable distribution for utilization of the sulphur; 65 per cent being available as a 2.91 per cent SO₂ gas in a volume of 485 cu. ft. per sq. ft. of hearth

SO₂ as a 2.38 per cent gas in 810 cu. ft. per sq. ft. of hearth area, as against 60 per cent as a 2.75 per cent gas in 480 cu. ft. for the 4-in. vacuum and 57.5 per cent as a 2.35 per cent gas in 500 cu. ft. for the 2-in. vacuum.

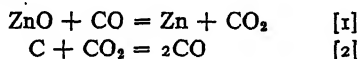
The maximum SO₂ concentrations obtained are lower than is usual when sintering a high-lead, high-sulphur charge. This is probably caused by the low sulphur content of the feed, together with the rather open character of the bed and the use of a bed only 4 1/2 in. deep instead of the deeper bed often employed in double sintering. As the primary consideration in sintering this material was to obtain the maximum sulphur elimination while making a first-quality sinter cake, with SO₂ concentration in the gases of secondary interest only, the shallower bed was preferred.

Relative Rates of Reactions Involved in Reduction of Zinc Ores

By E. C. TRUESDALE* AND R. K. WARING,* MEMBER, A.I.M.E.

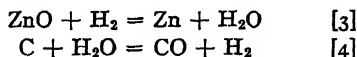
(New York Meeting, February 1941)

THE Research Division of The New Jersey Zinc Company (of Pa.) has conducted, over a period of years, numerous tests of the reducibility of various zinc ores and the reactivity of various kinds of coal, using a number of different experimental methods. Most of these tests have involved the reduction of mixtures of ore and coal. In such cases the following simultaneous reactions are believed to be mainly responsible for the production of zinc, as was shown by Bodenstein¹ some years ago:



Each of these reactions is dependent upon the other for the supply of CO and CO₂, respectively, and the over-all rate of formation of zinc vapor will be determined by the slower of these two reactions.

An analogous pair of reactions sometimes of importance is:



While it is possible to obtain an indication of the relative reducibility of various ores, or of a fine versus a coarse ore, by testing them with a given coal, and while coal reactivities may be measured in a corresponding manner, a more direct

determination of relative reaction rates is possible by carrying out the desired reactions, such as 1 and 2, separately and under reproducible conditions. It is one purpose of this paper to present some of the results that have been obtained by the latter method.

C. G. Maier² discusses the relative rates of reactions 1 and 2 and concludes that while at relatively low temperatures reaction 1 is faster than reaction 2, this difference becomes less with increasing temperatures, although at smelting temperatures reaction 1 is still the faster. He also says (p. 48), "At temperatures . . . between 1100° and 1300°C., . . . the zinc oxide reduction reaction is intrinsically more rapid than its physical limitations; that is, it is limited by gas diffusion rates."

In the course of numerous reactivity tests involving the separate use of reactions and 1 and 2, we have obtained data that show by direct experiment, we believe for the first time, the correctness of Maier's statements concerning these reactions. We also include data on the relative rate of reaction 3, involving reduction by hydrogen. Finally, some interesting results obtained by carrying out the reduction of a zinc ore-coal briquet in streaming atmospheres of nitrogen, carbon monoxide and hydrogen, respectively, are presented.*

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* Research Division, The New Jersey Zinc Company (of Pa.), Palmerton, Pa.

¹ References are at the end of the paper.

* The method described in this paper for measuring gaseous reaction rates has also been modified to obtain equilibrium data for the ZnO-CO reaction, and the results will appear in the *Journal of American Chemical Society*.

EXPERIMENTAL PROCEDURE

Experimental Method.—The experimental method adopted for the determination of the respective reaction rates was to pass a stream of the desired gas at a known rate through a vertical furnace tube, which was maintained at the desired temperature and in which a small briquet of the desired solid reactant was freely suspended from one arm of an analytical balance. By determining the rate of loss in weight of the briquet for successive brief intervals the course of the reaction could readily be depicted by plotting this reaction rate, in mols per minute, against time. The use of standard rates of gas flow and of briquet size permitted the determination of the effect on the reaction rate of changes in gas composition, temperature, and the character of the solid reactant; these standardized experimental conditions also permitted a direct comparison of the rates of the various chemical reactions. These rates, as usual in reactions involving solids, are influenced by the effective specific surface of the materials. The effective specific surface depends not only on the measured area of the briquet but also on factors such as particle size and porosity. The relative rates reported in this paper, therefore, apply quantitatively only to the particular materials used. It is believed, however, that they give a rough measure of what is to be expected with other materials of a similar nature.

Apparatus.—The furnace used was a compensated wound laboratory furnace, 17 in. long by 12 in. in diameter, provided with a silica reaction tube $1\frac{1}{4}$ in. in diameter and 30 in. long, the bottom end of this vertical tube projecting 6 in. below the lower end of the furnace. Immediately above the upper end of the furnace a $\frac{3}{4}$ -in. diam. silica side tube was sealed onto the reaction tube, wound with resistance wire for heating, and insulated. The purpose of this auxiliary heating was to keep the exit

gases hot, thus preventing the condensation of zinc or excessive formation of rock oxide. A hydrogen flame was usually kept at the mouth of this tube. The furnace was mounted on a small truck to facilitate alignment with the balance so that the briquet would be freely suspended.

Fig. 1 shows the arrangement of the reaction tube assembly and the location of the experimental briquet. Unimportant sections of the tube have been omitted from the figure, in order to permit reproduction of the essential features of the assembly. The system of tubes, held in place by rubber stoppers, *C*, which were thermally insulated by plugs *D*, was arranged so that by passing a stream of purified nitrogen into the upper side arm *B* a downward current of inert gas was created, which prevented any of the gaseous reaction products from leaving the furnace except through the heated side tube *F*. This arrangement was necessary to prevent condensation of zinc or zinc oxide on the $\frac{1}{16}$ -in. silica rod *A*, by which the specimen briquet *H* was suspended from the overhead balance. *K* was a baffle used to spread the incoming reducing gas, and *J* was the refractory protection tube for the platinum-platinum-rhodium thermocouple.

Composition of Materials.—The composition of the zinc-bearing materials used in

TABLE I.—*Composition of Ore Samples Used for Reduction Tests*

Material	Composition, Per Cent						
	Zn	Fe	Mn	Pb	S	CaO	SiO ₂
Roasted flotation concentrate.....	68.1	2.35		3.3	1.5		
Selected willemite ^a	50.7	0.3	6.2			0.22	26.6
Pigment zinc oxide.....	80+	0.015		0.02	0.03 (as SO ₃)		

^a The composition of pure willemite is theoretically 58.7 per cent Zn, 26.8 per cent SiO₂. The selected willemite must, therefore, have contained some tephroite, Mn₂SiO₄.

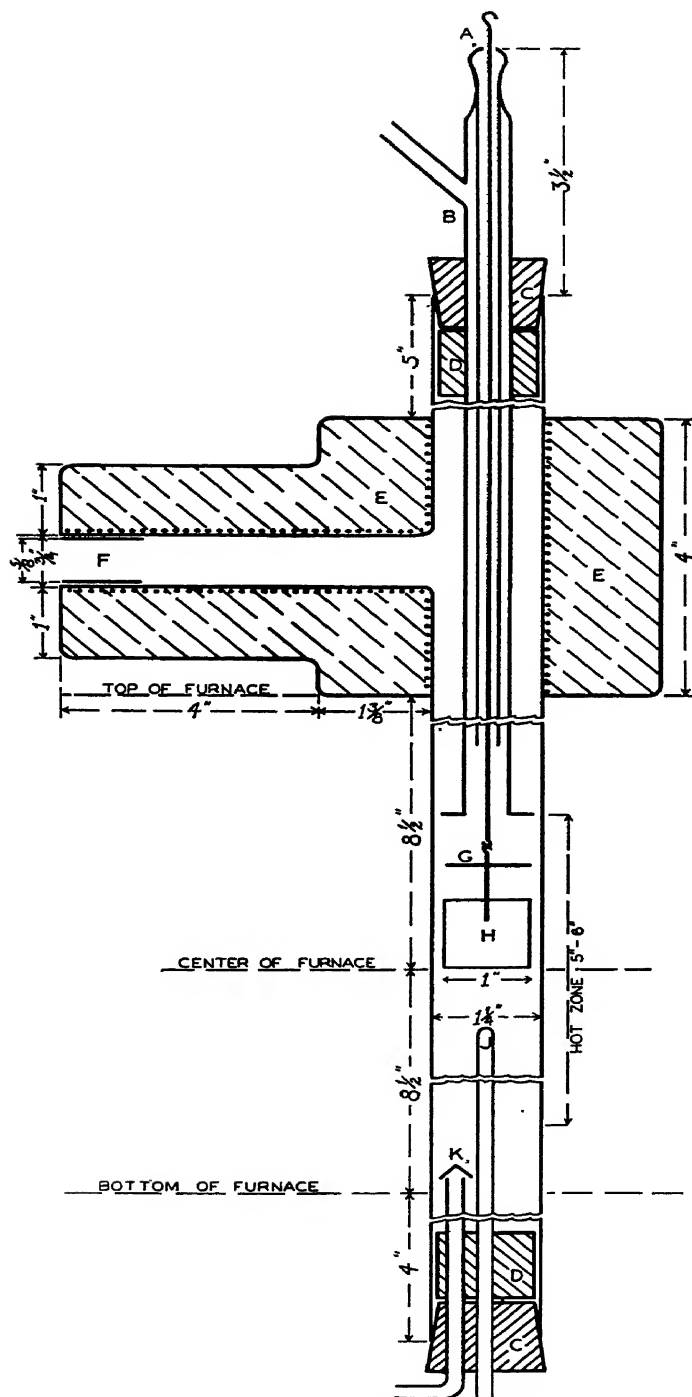


FIG. 1.—FURNACE TUBE FOR GASEOUS REDUCTION TESTS.

these tests is given in Table 1. The first ore was a commercially roasted flotation concentrate, crushed to pass 200 mesh. The second ore consisted of hand-picked

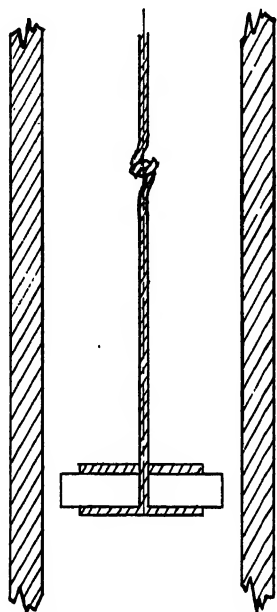


FIG. 2.—ARRANGEMENT OF $\frac{1}{4}$ -INCH BRIQUETS IN FURNACE.

crystals of willemite obtained from the Franklin, N. J., mine, and was also crushed to pass 200 mesh. The third material was a relatively coarse, ceramic-grade pigment oxide, which was selected instead of purer oxides because it underwent negligible shrinkage when heated in briquetted form.

The bituminous coal that was used was coked before being crushed to pass 100 mesh and made into briquets. The coked material contained 15.7 per cent ash, and 3.2 per cent sulphur. A complete ash analysis was not made, but the total alkali metal content, reported as Na, was about 0.2 per cent for the briquetted and recoked material. The ash analysis is important in connection with the catalytic effect of alkali metal compounds on the rate of the carbon-carbon dioxide reaction.

The Acheson graphite used came from

coarse-grained commercial rods. Its use was abandoned when results obtained at one or two temperatures indicated that constituents of widely different reactivities were present. A pure variety of graphite would undoubtedly have indicated a smaller reactivity.

The activated charcoal with which experiments were made at only two temperatures was a commercial variety made by the pyrolysis of waste solutions of cellulose; it was said to contain more than 98 per cent carbon and to have a very low ash content.

Purification of Gases.—The gases used in the investigation were carefully purified and dried by conventional means. Particular attention had to be paid to removal of sulphur present as carbonyl sulphide in the carbon monoxide. This was because carbonyl sulphide tended to form a film of zinc sulphide on the briquet.

The rates of gas flow were measured by means of carefully calibrated capillary flow meters.

Preparation of Briquets.—All briquets were made on a small laboratory press. Water was a suitable liquid to add in pressing the ore briquets, but with the carbon briquets a dilute honey solution was found to work more satisfactorily as a binder. All briquets were dried and then heated at 1000°C. for one hour; this served to harden them to the necessary degree and with the coal also served to drive off additional volatile matter. Ore briquets were heated in air, carbon briquets in purified nitrogen. Graphite pieces were machined to the standard briquet size.

Some of the first experiments were done with the 1-in. briquets shown in Fig. 1, and longer ones were used on occasion, but it was soon found that the reaction rates were too rapid for convenient measurement, and that the reaction was being slowed down by its close approach to equilibrium. Accordingly, the length of the 1-in. dia. briquet was reduced from 1 in. to $\frac{1}{4}$ in. and the

disk thus formed was mounted between two circular silica plates approximately $\frac{1}{8}$ in. in diameter, thus exposing a ring of the briquet $\frac{1}{4}$ in. thick and $\frac{1}{8}$ in. wide to the reacting gas. A rapid gas flow was thus maintained in the $\frac{1}{8}$ -in. annular space separating the briquet from the furnace tube. This arrangement is illustrated in Fig. 2. Unless otherwise mentioned, all data refer to the $\frac{1}{4}$ -in. briquets. The apparent exposed area of these briquets was 7.5 sq. cm. and the "time of contact" of the hot gas and briquet was of the order of 0.01 sec. The reproducibility of the reaction-rate measurements with these $\frac{1}{4}$ -in. thick briquets was about 5 per cent in most cases.

Description of a Typical Experiment.—The furnace was surveyed and the temperature adjusted before the beginning of a series of experiments, so as to give a zone of uniform temperature about 5 in. long, the center of which was slightly above the center of the furnace. The experimental briquet was suspended as nearly as possible in the middle of this zone. Temperatures were measured by a carefully calibrated platinum-platinum-rhodium thermocouple inserted from the bottom of the furnace to a point about 1 in. below the briquet, as at *J*, Fig. 1, and the furnace temperature was maintained constant to $\pm 1^\circ$ by an automatic controller. The temperatures thus measured were higher by a few degrees than the temperature of the reacting surface of the briquet, since the reactions being studied were strongly endothermic. A few experiments were made to determine this temperature difference and will be described later.

In starting an experiment, the briquet was suspended in the furnace until it attained a constant temperature and an approximately constant weight. During this time, a stream of 2000 c.c. per minute of purified nitrogen was passed through the furnace, and an equal flow of nitrogen into the upper end of the reaction tube was

maintained throughout an experiment. Ore briquets quickly reached a constant weight while coke briquets, because of further loss of volatile, required about $\frac{1}{2}$ hr. to attain a weight loss as low as 1 or 2 mg. per min., which usually was negligible in comparison with the reaction rate to be measured.

With the briquet and suspension balanced, the experiment was finally begun by shutting off the flow of nitrogen at the bottom of the furnace and admitting the desired gas. The rate of weight loss was determined by successively removing fractional gram weights from the balance and then determining, with a stop watch, the times at which the pointer passed the zero mark. The record of a typical experiment is given in Table 2, in which the rate of weight loss, measured in grams per minute, has been expressed in mols per minute in order that the results obtained with different materials may be directly comparable.

TABLE 2.—*Typical Experiment*

Briquet of roasted flotation concentrate reduced at 1000°C., using CO at the rate of 2000 c.c. per min. Weights removed from balance pan in steps of 0.2 gram each. Gas contained 99.5 per cent CO, 0.5 per cent N₂.

Total Time, Min.	Time Intervals, Min.	Reaction Rate, Mols per Min.
0.0		
0.57		
1.30	0.73	0.0034
2.10	0.80	0.0031
2.97	0.87	0.0028
3.87	0.90	0.0027
4.82	0.95	0.0026
5.80	0.98	0.0025
6.83	1.03	0.0024
7.89	1.06	0.0023
9.00	1.11	0.0022
10.12	1.12	0.0022
11.30	1.18	0.0021
12.55	1.25	0.0020
13.87	1.32	0.0019
15.22	1.35	0.0018
16.67	1.45	0.0017

Estimation of Reaction Temperatures.—

It was realized that the temperature of the briquet surface would drop rapidly following the start of an experiment, and probably would become fairly constant at some lower value within a few minutes. This

drop in temperature should be greater, the more highly endothermic the reaction, the more reactive the substance being tested, and the higher the experimental temper-

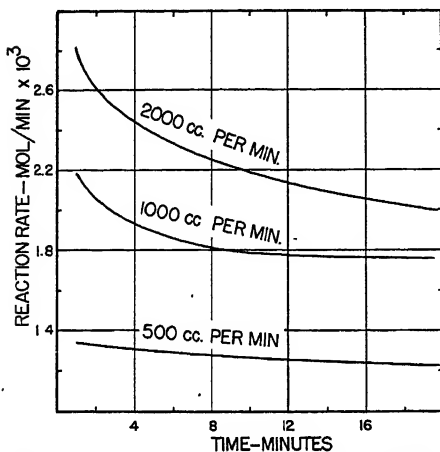


FIG. 3.—RATE OF REDUCTION OF ZINC OXIDE BY CARBON MONOXIDE AT 900°C.
Briquet diameter, 1 inch; length, 0.8 inch.

ature. This uncertainty concerning briquet temperature was probably the most serious one encountered in the course of the work.

The small size of the $\frac{1}{4}$ -in. test briquets precluded any measurement of briquet temperature under test conditions, but some tests were made on longer, unshielded zinc-ore briquets which served to show the order of magnitude of the temperature drop occurring during the reduction of zinc ores. A platinum-platinum-rhodium thermocouple in a $\frac{3}{16}$ -in. silica protection tube was embedded along the axis of a briquet so that the couple junction was $\frac{1}{2}$ in. from the bottom of the briquet. Nitrogen was run through the furnace until this couple and the control couple below the briquet reached the same temperature. Carbon monoxide was then run through the furnace until a constant temperature difference was indicated by the two couples; this required from 10 to 20 minutes.

Results obtained with pure willemite briquets 1 in. long showed a drop in

briquet temperature of 3° at 1000°C. and of 6° at 1100°, and the same results were obtained whether the carbon monoxide flowed at 200 or 2000 c.c. per min. This independence of rate of gas flow would be expected of a slowly reacting material.

Results obtained with zinc oxide briquets were as follows: At 1000°C., 1-in. briquets showed temperature drops of 12° and 27°, respectively, when the rate of gas flow was 200 and 2000 c.c. per min. At 1100°C., briquets $1\frac{1}{4}$ in. long showed temperature drop of 8° and 24°, respectively, when the rates of gas flow were 200 and 2000 c.c. per min. No tests were made with the remaining zinc ores, but the drop in briquet temperature undoubtedly would be proportional to the reactivity of the materials. Similar proportional decreases in briquet temperature would be expected for the carbonaceous materials, since the heat requirement of the CO-CO₂ reaction is of the same order of magnitude as that of the ZnO-CO reaction.

Since the reaction rates will be shown to be approximately doubled for a 100° rise in temperature, it is obvious that the decrease in briquet temperature that must have occurred during the first 10 or 15 min. of an experiment would be accompanied by an appreciable decrease in reaction rate, and that the more reactive materials would be more severely penalized in this respect. It is for this reason that, in the majority of cases, *initial* rates, obtained while the briquets were still at the nominal furnace temperatures, were used in determining relative reaction rates.

EXPERIMENTAL RESULTS

Effect of Rate of Gas Flow.—The effect of the rate of gas flow on the reaction rate is shown in Fig. 3. These results were consecutively obtained with a briquet 0.8 in. long, the curves being shifted for convenience to a common time origin, and show clearly that with so large an exposed surface a significant approach to equilibrium

had occurred, so that a satisfactory approach to a maximum reaction rate could not be obtained at permissible gas velocities. This is a consideration frequently

partly because with this ore an inert residue remained through which the gas must diffuse to get at the unreduced ore. Formation of a porous residue should be even

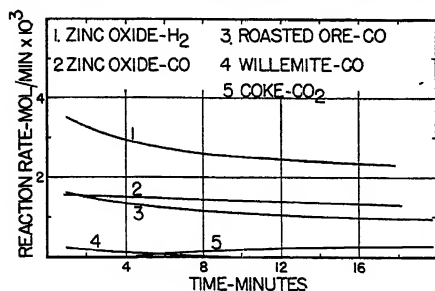


FIG. 4.—RATES OF REACTION AT 900°C. OF $\frac{1}{4}$ -INCH BRIQUETS IN A GAS STREAM FLOWING AT 2000 CUBIC CENTIMETERS PER MINUTE.

overlooked in reaction-rate measurements. The curves also show that the decrease with time of the initial reaction rate was much greater with a faster gas flow. This decrease in rate must be largely ascribed to the decrease in briquet temperature following the start of the reaction, but it is also due in part to the progressive decrease in the size of the briquets, and in part to the formation of gas films at the briquet surface through which counter-diffusion must occur.

In the remaining data to be presented on gaseous reduction rates, the $\frac{1}{4}$ -in. briquets of Fig. 2 were used, and the rate of gas flow was held at 2000 c.c. per minute.

Effect of Temperature on Reaction Rate.—Figs. 4, 5 and 6 show the curves of reaction rate versus time for some of the materials at furnace temperatures of 900°, 1000° and 1100°C., respectively, all plotted to the same scale. Each curve is the average of two or more experiments.

There are several points of interest in these curves. The initial rates for zinc oxide and the roasted flotation concentrate were nearly identical; but the latter decreased with time more rapidly, partly because the initial rate for the latter material was too high as a result of the rapid reduction of lead and iron oxides, and

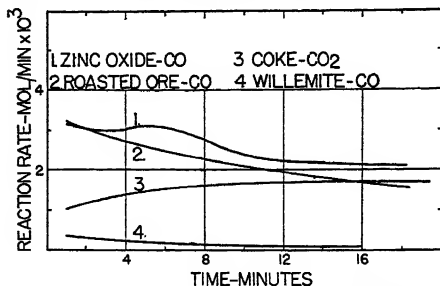


FIG. 5.—RATES OF REACTION AT 1000°C. OF $\frac{1}{4}$ -INCH BRIQUETS IN A GAS STREAM FLOWING AT 2000 CUBIC CENTIMETERS PER MINUTE.

more serious in the reduction of willemite, and the fact that the decrease in rate with time was not there more pronounced probably indicates that the inherent reaction

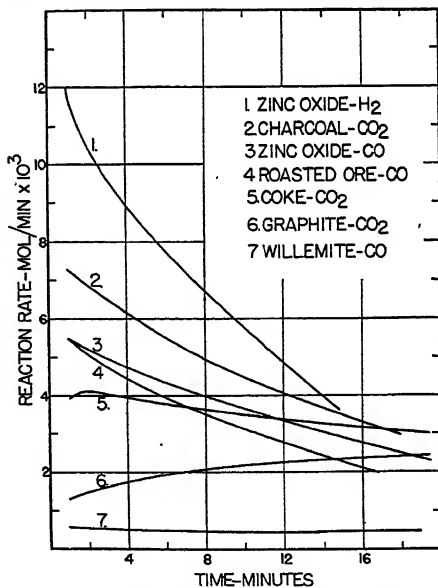


FIG. 6.—RATES OF REACTION AT 1100°C. OF $\frac{1}{4}$ -INCH BRIQUETS IN A GAS STREAM FLOWING AT 2000 CUBIC CENTIMETERS PER MINUTE.

rate of willemite was not greater than the gaseous diffusion rates.

The peculiar kink in the zinc oxide curve at 1000° was observed in all five of the ex-

periments made at this temperature, but no explanation of this phenomenon has been found.

The rate of reduction of carbon dioxide

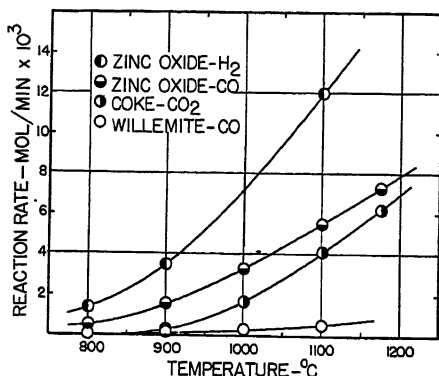


FIG. 7.—MAXIMUM REACTIVITY AS A FUNCTION OF TEMPERATURE.

by coke increased with time at the two lower temperatures, but decreased with time at 1100°. The first result is believed to be due to the catalytic effect of the coke ash in promoting the reaction, while the reverse effect at 1100° indicates that diffusion phenomena were controlling the rate of even the catalyzed reaction.

From the apparent equality of the rates for the roasted ore and for coke, which was attained in about 15 min. at 1000° and in an even shorter time at 1100°, one might conclude that a similar equality of rates would hold in a "steady-state" condition in a commercial retort. But such a conclusion is not necessarily correct, since only the initial rates are measured under comparable conditions, and since there is no assurance that equal surface areas of ore and coal are available in a commercial retort charge.

The curves of Figs. 4, 5 and 6 show clearly the great difference in reactivity between charcoal, coke and graphite, between an oxide type ore and a silicate ore, and between hydrogen and carbon monoxide.

From the curves of Figs. 4, 5 and 6, and similar curves obtained at 800° and 1175°

for some of the materials, the initial rates taken 1 min. after the start of the reaction and the rates after 15 min. (representing an approach to a steady state) were read off and are recorded in Tables 3 and 4, together with the temperature coefficients for each 100° interval. These data are used in Table 5 to show the relative maximum reaction rates, with the rate for the reduction of zinc oxide by carbon monoxide being taken as unity at each temperature. In this table, the maximum rates are initial rates except that the 15-min. rates were used for the coke-carbon dioxide reaction at 900° and 1000°.

Fig. 7 shows the maximum reactivity of the coke and the three zinc-bearing materials plotted as functions of temperature, the data being taken from Tables 3 and 4.

TABLE 3.—Rate of Reduction of Zinc-ore Briquets

Rate of gas flow, 2000 c.c. per min. Initial exposed area of briquet, 7.5 sq. cm. Time of contact about 0.01 second.

Material	Temperature, Deg. C.	Average Reduction Rate, Mols per Min. of ZnO		Temperature Coefficient for Each 100° Interval	
		Initial	15 Min.	Initial	15 Min.
REDUCTION BY CARBON MONOXIDE					
Zinc oxide....	800	0.0006	0.0005		
Zinc oxide....	900	0.0016	0.0014	2.7	2.8
Zinc oxide....	1000	0.0031	0.0021	1.9	1.6
Zinc oxide....	1100	0.0055	0.0031	1.8	1.5
Zinc oxide....	1175	0.0073	0.0032	1.5 ^a	1.2 ^a
Roasted flota- tion concen- trate.....	900	0.0016	0.0010		
Roasted flota- tion concen- trate.....	1000	0.0032	0.0018	2.0	1.8
Roasted flota- tion concen- trate.....	1100	0.0055	0.0023	1.7	1.3
Willemite....	900	0.0002	0.00004		
Willemite....	1000	0.0003	0.0002	1.5	5.0
Willemite....	1100	0.0006	0.0005	2.0	2.5
REDUCTION BY HYDROGEN					
Zinc oxide....	800	0.0014	0.0011		
Zinc oxide....	900	0.0035	0.0024	2.5	2.2
Zinc oxide....	1100	0.0120	0.0035	1.7 ^b	0.7 ^b

^a Estimated from the 75° temperature interval.

^b Average 100° temperature coefficient over 200° temperature interval.

TABLE 4.—*Rate of Reaction of Carbon with Carbon Dioxide*

Rate of gas flow, 2000 c.c. per min. Initial exposed area of briquet, 7.5 sq. cm. Time of contact about 0.01 second.

Material	Temperature, Deg. C.	Average Reaction Rate, Mols per Minute of Carbon		Temperature Coefficient for Each 100° Interval	
		Initial	Maximum	Initial	Maximum
Bituminous coal, . . .	800	0.00005 ^a	0.00005		
Bituminous coal, . . .	900	0.00012 ^b	0.0003	(2.4)	6.0
Bituminous coal, . . .	1000	0.0010	0.0017	8.3	5.7
Bituminous coal, . . .	1100	0.0039	0.0041	3.9	2.4
Bituminous coal, . . .	1175	0.0063	0.0063	1.6	1.5
Graphite, . . .	1000	0.0003	0.0004		
Graphite, . . .	1100	0.0014	0.0025	4.7	6.2
Activated charcoal, . .	900	0.0011	0.0011		
Activated charcoal, . .	1100	0.0073	0.0073	(2.6) ^c	

^a First reading obtained about 15 min. after start of reaction.

^b First reading obtained about 8 min. after start of reaction.

^c Average 100° temperature coefficient over 200° interval.

TABLE 5.—*Relative Reaction Rates of Materials Used in Zinc Reduction*

Material	Reacting with	Maximum Reaction Rate Relative to Zinc Oxide				
		Temperature, Deg. C.				
		800	900	1000	1100	1175
Zinc oxide,	H ₂	2.33	2.19		2.18	
Zinc oxide,	CO	1.00	1.00	1.00	1.00	1.00
Roasted flotation concentrate, . . .	CO		1.00	1.03	1.00	
Willemite,	CO		0.13	0.10	0.11	
Activated charcoal	CO ₂		0.69		1.33	
Coked bituminous coal,	CO ₂	0.08	0.19	0.55	0.75	0.86
Graphite,	CO ₂		0.05 ^a	0.13	0.45	

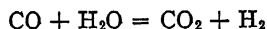
^a Estimated from preliminary data on larger briquets.

Effect of Gas Composition on Reaction Rate.

Space will not permit more than a brief description of experiments done to demonstrate the effect of gas composition on the rate of reduction of zinc oxide by carbon monoxide. Under reaction conditions far removed from equilibrium, nitro-

gen would be expected to act primarily as a diluent, and experiments at 1100° showed that with nitrogen additions up to 12 per cent, the reaction rate was decreased by approximately 2 per cent for each per cent of nitrogen added. Carbon dioxide, being one of the reaction products as well as a diluent, would be expected to be a more effective inhibitor, and experiments at 1100° showed that additions of up to 11 per cent of carbon dioxide were approximately twice as effective as comparable amounts of nitrogen in decreasing the reaction rate.

The effect of water vapor on the reaction rate was studied by alternately passing dry and moist carbon monoxide over a zinc oxide briquet under the standard test conditions. The vapor pressure of the gas was thus quickly and repeatedly varied from 0.8 to 18 mm., and it was found that the moist gas consistently reduced the reaction rate by from 10 to 18 per cent. This effect cannot be explained by assuming the gases to react to form carbon dioxide before reaching the briquet according to the equation:



since this reaction would not occur sufficiently at 1100°. No other explanation of the effect of water vapor has been found.

Discussion of Heterogeneous Reaction Rates.—The rate of a gas-solid reaction is determined by the number of reactant molecules striking unit surface per second and, since only a small fraction of such collisions are fruitful, by the efficiency of the collision process.* According to the collision theory, only those collisions are fruitful in which the sum of the available energies (kinetic, vibrational, etc.) of the colliding molecules exceeds the average molecular energy by an amount called the energy of activation, *E*. Since activation energies are usually very much larger

* An extensive exposition of this theory is given by Hinshelwood.²

than the average molecular energy, these are customarily lumped together and the reaction is assumed to be carried on by molecules having energy equal to or greater

absolute temperature:

$$N_E = N_0 \times e^{-E/RT}$$

Hence, the fraction N_E/N_0 , having such energy at a temperature T , is found by solving the equation:

$$\log N_E/N_0 = -0.4343E/RT$$

For a given value of E , the value of the fraction N_E/N_0 , may be computed at temperatures of interest, and the ratio of the values of this fraction at two temperatures gives the relative number of activated molecules at these temperatures, and this ratio should also equal the temperature coefficient of the reaction rate for the interval in question. The larger the value of E , the greater is the temperature coefficient of the reaction rate.

By plotting the logarithm of N_E/N_0 , or the logarithm of the reaction rate against $1/T$, a straight line should be obtained whose slope depends on the value of E . Three curves, corresponding to different values of E , are shown in Fig. 8, in which the lines have been arbitrarily shifted to have a common origin corresponding to $800^\circ\text{C}.$, and in which the relative values of the fraction N_E/N_0 are expressed as relative reaction rates. In the same figure, the logarithms of the experimentally observed reaction rates, taken from Figs. 4, 5 and 6 are plotted in order to permit comparison of the slopes of the various curves.

The production of a straight line on such a plot indicates that some one reaction mechanism is controlling the reaction rate. It happens frequently that a reaction proceeds by one mechanism in one temperature range and by another mechanism, requiring a different value of E , in a different range. In this case two straight lines of different slope should be obtained, curving into each other in the intermediate range where the two mechanisms are competing with each other. The curvature, at the higher temperatures, of the line representing the zinc oxide-carbon monoxide reaction,

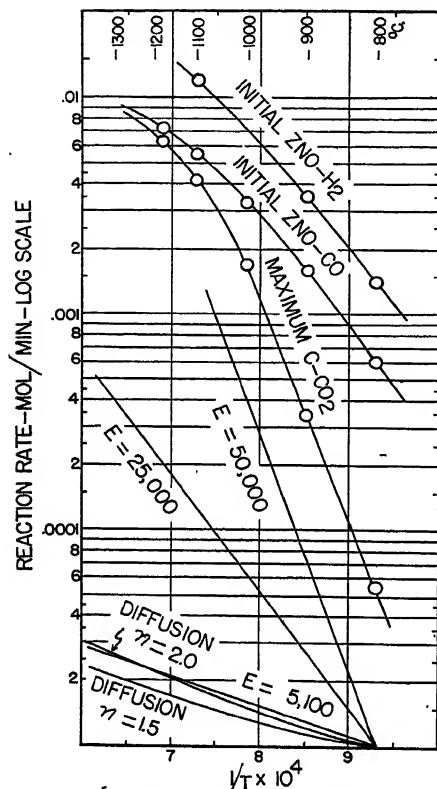


FIG. 8.—LOGARITHMIC PLOT OF REACTION RATES AGAINST THE RECIPROCAL OF THE ABSOLUTE TEMPERATURE.

than E calories per mol. The increase in reaction rate with increasing temperature, commonly called the temperature coefficient of the rate, is, therefore, a measure of the increase with temperature of the number of activated molecules. Thus, if the temperature coefficient is known, the value of E may be calculated, and *vice versa*.

The number of molecules, N_E , out of a total number, N_0 , having energies greater than E calories per mol is given approximately by the following equation where R is the molar gas constant and T is the

and of that representing the carbon-carbon dioxide reaction, is taken to mean that the molecular reaction mechanisms governing the respective reaction rates at low temperatures are being superseded by some other process requiring a lower energy of activation and having, therefore, a smaller temperature coefficient.

It is believed that this superseding mechanism is the relatively slow process of the diffusion of the reacting gas to the briquet surface through a film of counter-diffusing reaction products. The temperature coefficient of the diffusion rate of a gas may be given approximately by the expression:

$$D_2 = D_1(T_2/T_1)^n$$

where D is the diffusion coefficient, T is the absolute temperature, and the constant, n , varies from 1.5 for an ideal gas to about 2.0 for actual gases at high temperature. Calculation of relative diffusion rates from this equation for temperatures of present interest shows them to behave as though a process were occurring that required an activation energy of about 5100 cal. per mol; that is, an activation energy approximately equal to the average energy of a diatomic gas at 800°C. These curves are shown at the lower left of Fig. 8. If the assumption is correct that the experimental reaction rates are being limited by diffusion at high temperatures, the latter curves may be considered as representing the limiting slope that curves for the chemical reactions would approach at still higher experimental temperatures. It is of particular interest to note that the curve for the reduction of zinc oxide by hydrogen, a gas noted for its rapid diffusion characteristics, has not yet acquired a pronounced curvature at 1100°C; in other words, the diffusion rate is still so rapid that it is not limiting the inherent chemical reaction rate.

Effect of Gases on the Reduction of Ore-coal Briquets.—The fact that gaseous diffu-

sion rates are a limiting factor in the reduction of zinc ores is nicely shown by some experiments in which briquets 1 in. in diameter and 1 in. long, composed of 50 per

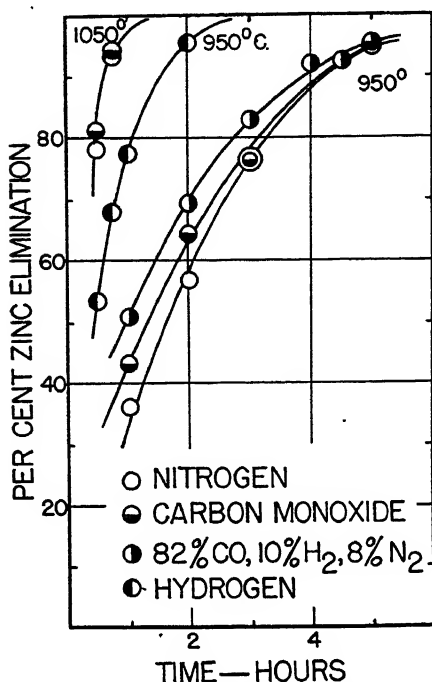


FIG. 9.—EFFECT OF FURNACE ATMOSPHERE ON REDUCTION OF BRIQUETS OF ZINC ORE AND COAL.

cent zinc oxide, 35 per cent crushed bituminous coal and 15 per cent anthracite dust were first coked at 600° to 900° in nitrogen and then reduced at various temperatures in flowing atmospheres of nitrogen, carbon monoxide and hydrogen, respectively. The furnace tube was 1¼ in. in diameter and the gases flowed at a rate of 1000 c.c. per min. Fig. 9 shows the curves of percentage of zinc elimination, based on chemical analysis, versus time, and Fig. 10 shows the relationship between zinc elimination and weight loss.

These experiments show that a stream of carbon monoxide is not more effective than a stream of nitrogen in the tests at 1050°, and that while carbon monoxide does increase the reduction rate at 950°, it is

effective only during the early stages of reduction. Carbon monoxide containing only 10 per cent of hydrogen is much more effective at 950°, and the effect on the

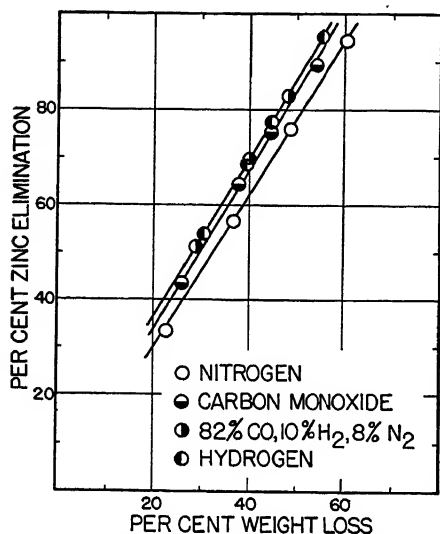


FIG. 10.—ZINC ELIMINATION VERSUS WEIGHT LOSS FOR THE REDUCTION DATA OF FIG. 9.

reduction rate persists until reduction is nearly complete. Pure hydrogen at 950° speeds up the reduction in a very striking manner, and remains effective until elimination of zinc is complete.

In a normal reduction process, the weight loss of the briquet is due to the disappearance of zinc oxide and carbon. If some reduction is due to added reducing gases, less carbon will be used and the weight loss for a given zinc elimination will be less (Fig. 10). While it is obvious from Fig. 9 that much of the reduction was due to hydrogen when this gas alone was used, the weight loss was not decreased in anything like the same proportion. This suggests that carbon was being used in some other reaction, and it is believed that the most likely reaction is the following, the water vapor coming from the reduction of zinc oxide by hydrogen:



These results indicate that carbon monoxide, a relatively slowly diffusing gas, when externally supplied aids the reduction of ore-coal briquets only at temperatures at which the diffusion rate is faster than the normal reduction rate, and even then only so long as reduction is occurring near the outer surface of the briquet where extensive diffusion is not required. Hydrogen, on the other hand, diffuses so rapidly that even the thickness of the almost completely reduced briquet offers very little resistance to its passage.

DISCUSSION OF RESULTS

Two general facts shown by the present experiments, that hydrogen is more reactive than carbon monoxide and that charcoal, coke and graphite are progressively less reactive forms of carbon, have, of course, been common knowledge for a long time, and the reasons for not employing charcoal and hydrogen in commercial zinc smelting are economic ones. Unfortunately, it is not feasible to employ hydrogen in a divided process in which hydrogen is used to reduce zinc oxide in one retort and is regenerated by the reduction of water vapor by coke in a second retort, since in each cycle the hydrogen would be diluted with an ever-increasing volume of carbon monoxide by virtue of the water-gas and producer-gas reactions.

Since the carbon-carbon dioxide reaction has been shown to be the slower of the two reduction reactions at low temperatures, any effort to speed up zinc reduction early in the smelting cycle should be directed toward acceleration of this reaction. At the higher temperatures existing toward the close of a cycle, the rates of both reactions are nearly equal and both are limited by diffusion, so that it is the diffusion processes that then need to be accelerated.

Numerous data in the literature show that substances such as sodium carbonate catalyze the carbon-carbon dioxide reaction

at relatively low temperatures, but the effect decreases with increasing temperature and is negligible at normal zinc-smelting temperatures. The use of a catalyst does not alter the equilibrium requirements of the system, so that the maintenance of an abnormally low temperature throughout a smelting cycle in order to benefit from a catalyzed charge would probably result in a lowered concentration of zinc vapor and in increased condensation difficulties.

The possibility of accelerating the diffusion rates of carbon monoxide and dioxide at normal smelting temperatures appears to be remote. A less nebulous but still impractical remedy for the diffusion limitation would be the substitution of reactive and rapidly diffusible hydrogen in place of carbon monoxide, as previously mentioned.

A word of caution should be offered in connection with the possible interpretation of the data given in this paper. The experiments were done in a thin-walled silica tube, and the furnace represented an almost instantly available source of heat supplied at the experimental temperature. Such conditions do not hold in commercial retorts, where the heat required for the endothermic reactions must be transmitted through a relatively thick retort wall and, on the average, through a considerable thickness of charge. Thus, while it is still true that the rate of the carbon-carbon

dioxide reaction limits the over-all rate of zinc production, this is in commercial practice a secondary limitation dependent primarily upon the rate at which heat can be transferred to the charge.

ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of other members of the Research Division of The New Jersey Zinc Co. in this work, particularly that of Mr. Dale M. Smith, who performed many of the experiments.

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2. C. G. Maier: *U. S. Bur. Mines Bull.* 324 (1930) 48-50.
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DISCUSSION

(Herbert R. Hanley presiding)

O. C. RALSTON,* Washington, D. C.—This paper is an important addition to the literature on reaction kinetics of zinc reduction. The scientific literature on zinc reduction in the past concerns itself mainly with equilibrium data, established as the ideal criteria when unlimited time is available to reach equilibrium. This paper adds very considerably to an understanding of the various reaction rates involved and points out the steps that seem to be the slowest or limiting steps.

* U. S. Bureau of Mines.

Design and Operation of the Bunker Hill Slag-treatment Plant

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G. W. DUNN§

THE new Bunker Hill slag-treatment plant, designed for a capacity of 300 to 400 tons of hot slag per day, was "blown in" April 5, 1943. In the ensuing 15-months period, 157,530 tons of slag was processed, with an average recovery of over 90 per cent of the zinc and practically all of the lead contained.

In addition to this high metal recovery, utilization of the waste heat in the gas and fume venting, the process has enabled the generation of 231,376 tons of steam at 250-lb. gauge. Over the first six months operation the volume of slag treated averaged somewhat under 300 tons per day. Reclaimed dump slag made up only about 15 per cent of the plant feed.

In October 1943, preparations for the smelting of additional tonnages of dump slag were completed and the plant capacity was increased to an average of about 420 tons of slag per day. During the nine-months interval since that date, monthly averages of 450 tons per operating day have been maintained several times.

The new plant (Fig. 1) is constructed in close proximity to blast-furnace operations. The fuming furnace and other necessary equipment are housed in an eastward

extension of the existing blast-furnace building. Beyond this housed extension the dust-laden gas is conveyed about the perimeter of a large rectangle formed by the flues, cooling towers and baghouses. The course of a 10-ft. balloon flue, which transports the fuming furnace gas, describes the west and south perimeters. This flue connects with a set of cooling towers located at the south-east corner. The flue and cooling-tower system serving the deleading kiln constitute the north side and the two baghouses, serving the kiln and furnace operations, border the east side. From these baghouses the several discharge gas flows are combined and conveyed into the rectangle, being vented to atmosphere by means of a fan through a centrally located 200-ft. brick stack.

In general, the plant design and operation follow quite closely that dictated by experience gained in years of slag-fuming practice by the Anaconda Copper Mining Co., at East Helena, Mont., and the Consolidated Mining and Smelting Co. of Canada, Ltd., at Trail, B.C., and more recently by the International Smelting and Refining Co. at Tooele, Utah.

Fuming operations at the East Helena and the Tooele plants are more or less identical. Trail practice differs chiefly in the methods employed for the storage of the hot feed slag and in the methods utilized for the handling and cooling of the fuming furnace gas. The new Bunker Hill fuming plant closely follows Trail procedure in the treatment of the furnace discharge gas while East Helena methods have been adopted for the storage of feed slag.

This paper in part follows the text of an earlier paper published in the *Mining Congress Journal* (Oct. 1943). However, the production and metallurgical data have been brought up to date and changes in practice have been recorded. Manuscript received at the office of the Institute Aug. 8, 1944.

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Thus, instead of using a pulverized-coal-fired holding furnace as at Trail, the blast-furnace slag is stored in pots between fuming cycles. On the other hand, a waste-

3. The dust throughout the entire circuit is mechanically discharged, as produced, and continuously conveyed from the system

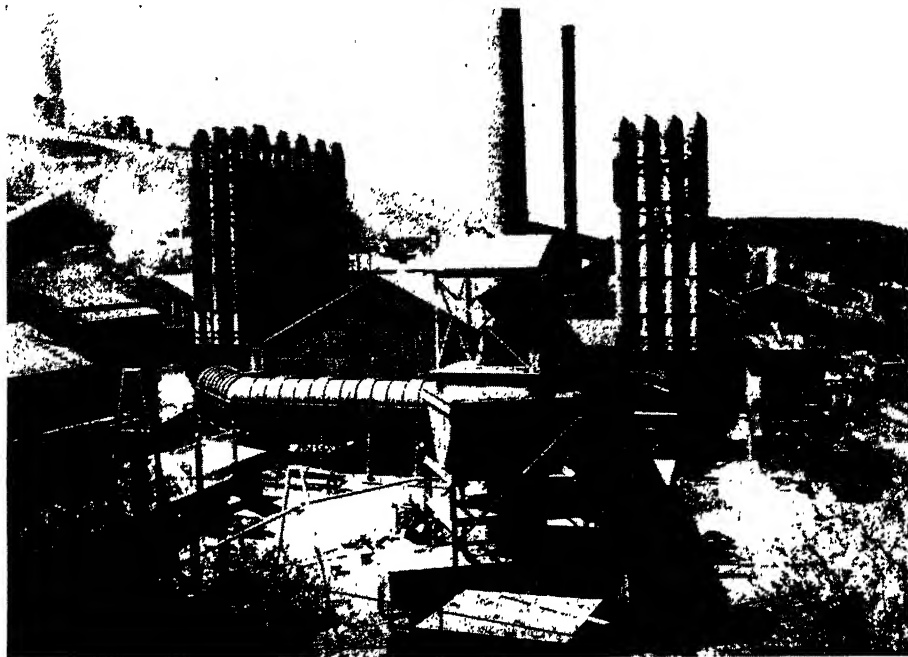


FIG. 1.—BUNKER HILL SLAG-TREATMENT PLANT.

heat boiler, economizer, and automatic baghouse are employed as in the installation at Trail. However, in certain departures from previous fuming-plant design and practice, the Bunker Hill smelter has successfully introduced the following innovations:

1. In contrast to the indirect pulverized-coal feeding systems utilized in previous installations—that is, the operation of a separate coal-pulverizing plant from which the pulverized coal is delivered to the fuming furnace through intermediate screw-discharged coal-storage hoppers—a direct pulverized-coal firing system is employed.

2. Instead of a multiple fan system for the transportation of discharge gas, the new plant employs a single fan operating in clean gas, after the baghouse, at the base of the stack.

4. The steam generated from the waste heat venting the furnace is not only utilized outside the plant but also within the operation for the driving of blowers, boiler-water feed pumps, and the stack fan. These innovations will be related in detail in the subsequent description and discussion of plant design and operation.

FUMING-PLANT DESIGN AND GENERAL PRACTICE

Fuming Furnace and Charging Procedure

As indicated in the foregoing paragraphs, the hot feed slag for treatment is tapped from the blast furnace into pots for storage between fuming cycles. Cast-steel pots of $6\frac{1}{2}$ tons capacity are used. These are transported by crane to and from a spacious concrete storage platform below and west of the fuming furnace. Upon comple-

tion of a fuming cycle the pots are elevated, transported, and dumped by crane through the charge hole of a slag-fuming furnace of standard water-jacket construction,* 15 ft. long by 8 ft. wide. The frozen slag shell, adhering to the pot walls, is dumped by crane into a clean pot or skip, upon completion of the furnace-charging operations. The broken shell, which comprises about 20 per cent of the hot slag received, is circulated for remelting through the blast furnace.

Direct Coal-feeding System

The coal and air are continually supplied through 28 double-inlet tuyeres, 14 on each side of the furnace. The pulverized coal is supplied directly by two of three standard type E, size 26, Babcock and Wilcox pulverizers, each of which has a rated capacity of 4080 lb. of coal per hour, grinding to a fineness of 82.6 per cent through 200-mesh when operating on a 50 grindability coal. Nos. 1 and 3 pulverizers are normally in service, with No. 2 as a standby to replace either of the others when necessary. No. 2 pulverizer can also be used to fire an auxiliary standby boiler when not in use on the fuming furnace. Burner-line piping and controls are so arranged that such changes may be made by simply manipulating three-way valves, a matter of a few minutes time. Each pulverizer is equipped with two 6-in. burner lines, each line serving seven tuyeres, or 14 tuyeres per pulverizer (one side of furnace).

The type E pulverizer utilizes the ball-bearing principle of grinding with grinding elements similar to a large ball thrust bearing. The pitch diameter of the races is 26

in. and eight 9¼-in. diameter balls are used. The races are made of chilled iron and the balls of hardened steel. The bottom race rotates at 165 r.p.m., whereas the top race is stationary and is spring-loaded usually to 1000 to 1200 lb. per ball, depending on the grindability of the coal. The thrust of the bottom race is taken through the main drive shaft to the main thrust bearing in the gear case, which forms the base of the pulverizer. The pulverizer is direct-driven through a bevel and pinion gear in the gear housing by a 30-hp. motor.

Raw coal is fed to the pulverizer by a table-type feeder, which is controlled automatically by the quantity of primary air, thus maintaining a constant air to coal ratio for any given load, and the primary air rate is controlled by adjusting the flow of air by dampers. The raw coal is fed to the pulverizers "as received," the pulverizing and drying taking place simultaneously in the grinding zone of the unit. Drying is accomplished by preheating the air to the pulverizer with steam heaters—the temperature required being dependent upon the quantity of surface moisture in the coal. Present normal requirement, with raw coal averaging about 3.5 per cent total moisture, is 280°F. air to maintain 200°F. pulverizer temperature with dryness down to less than 1 per cent total moisture. A rotating classifier, driven directly by the main shaft, is incorporated in the pulverizer design. In passage through this unit the coarse coal is separated and returned to the grinding elements, the finished coal being carried by the air stream into the burner lines.

For the task of feeding coal to the pulverizer units against internal operating pressures up to 10 lb. per sq. in., 7-ton conical equalizing bins are used. Each pulverizer is provided with a separate charging system, consisting essentially of two bins, one mounted above the other. The lower bin, of 8 tons capacity, is connected directly to the pulverizer feeder.

* The construction of the fuming furnace proper is, for all practical purposes, identical with that installed at East Helena, Mont. The jacket water, however, is circulated in a thermosiphon system, and alterations in the design of the Laist tuyere were necessitated by the adoption of the direct pulverized-coal feeding system. Also, because of the lack of adequate headroom between the existing craneway and the necessary furnace elevation, the charging spout was installed at a lower level than that used in the East Helena design.

This bin, receiving air from the same source, is always maintained at the same pressure as the pulverizer. Raw coal* is delivered by belt conveyor from an intermediate surge hopper to the upper equalizing bin. The coal flow is stopped when a fixed elevation is reached, as signaled through a light circuit activated by a level indicator. The inlet of the upper bin is then sealed by means of a conical valve and a three-way pressure-equalizing valve is operated to increase the internal pressure.

When the pressures in the upper and lower bins become equalized, permitting the opening of an intermediate sealing valve, the coal load discharges into the lower bin. When the coal surface eventually falls below the elevation of a level indicator in the lower pulverizer bin, as shown by a second signal light, the intermediate sealing valve is closed, the upper bin vented to atmosphere, the coal-inlet sealing valve opened, and the charging procedure repeated.

The automatic coal-charging system† of the initial plant installation was replaced by the manually operated arrangement just described. The original 800-lb. capacity equalizing bins proved too small; about 125 coal-charging cycles were required per day. Advantages of automatic operation were soon offset by the excessive attention necessitated by wear of moving parts, particularly with regard to the bin-sealing valves. In addition, ready estimates of coal consumption were impossible. The recording, scale-type feeders originally used were

unsatisfactory because of the lack of free flow from the raw-coal surge bins. The present arrangement requires an average of but two coal-charging cycles per shift and coal consumption is continuously recorded by Bailey coal meters, installed in the bin discharge chutes, which feed the pulverizers.

Operation to date of the direct coal-firing system has been very gratifying, no lost furnace time having been attributed to this source. The replacing of No. 1 or No. 3 unit with the standby, No. 2, has been accomplished on numerous occasions without incident or difficulty. The performance of the pulverizers and associated control equipment is unaffected by pressure changes within the process (between 1 lb. and $7\frac{1}{2}$ lb. per sq. in.). The coal-air ratio is maintained constant and a very uniform rate of coal delivery to the furnace tuyeres has been experienced. Positive variations in the coal rate are readily attainable by changing the volume of primary air to the pulverizers through the simple manipulation of a selector valve. The pulverizer coal output is then automatically adjusted by a Bailey feed control meter to compensate for the change in primary air volume effected.

Slag Treatment

Thus, in slag-treatment operations at the Bunker Hill smelter the coal is delivered to the furnace tuyeres from the pulverizers directly in a primary air stream comprising about 48 per cent of the total air flow. The remaining 52 per cent enters the tuyeres as secondary air. Two Ingersoll-Rand turboblowers, maximum rating 6910 cu. ft. per min. each at 8-lb. gauge, 5700 r.p.m., supply the furnace air. These are driven by 300-hp. Terry steam turbines operating at 235 lb. pressure and 27 in. Hg vacuum. The suction pipes leading to each of the blowers are fitted with metering orifices to record air flow. The blower pressure varies with the depth of slag in the fuming fur-

* Incoming coal is dumped from cars into a 40-ton coal bunker immediately north of the fuming plant. From this bunker it is conveyed and elevated to a concrete storage bin, composed of four 100-ton hoppers compartments, constructed on the south side of the building. A conveyor and elevator system distributes the coal from storage to intermediate 6-ton steel bins serving the pulverizers. The coal flow from these intermediate bins is weighed as delivered to the small equalizing hoppers that feed the pulverizer hopper.

† The original coal-charging system is described in the article in the *Mining Congress Journal* (Oct. 1943) mentioned on page 110.

nace. An Askania steam-turbine control, arranged to maintain a constant air flow against variable pressures, takes its impulse from the metering orifice.

The reduction of ZnO by CO gas is much more efficient than by solid carbon. Also, the maintenance of slag fluidity requires the partial combustion of most of the coal. Hence the minimum air supplied at the tuyeres approaches that required to burn the coal to CO gas. Less air than this requirement will result in inefficient reduction and, if carried to an extreme, the freezing of the furnace charge. As the air supply is increased beyond the requirement for CO, greater portions of CO₂ are formed within the bath. This trend results in higher slag temperatures and poorer metal reduction. Thus, the coal-air mixture forced through the slag bath supplies heat and effects the reduction not only of zinc oxide but also of the lead oxide contained. Within the churning slag bath the greater part of the coal burns to CO and it is generally accepted that the bulk of the reduction occurs at the boundaries of the CO bubbles. The reduced metal distills from the slag and is carried in the gas stream venting the furnace.

The slag is treated in batches, each batch comprising a furnace cycle. Each cycle, in turn, is divided into three periods—a charging period, a blowing period, and a tapping period. The designation of the second stage of the cycle as the blowing period is somewhat confusing in that the coal and air are actually delivered to the tuyeres continually throughout all operations. The charging and tapping periods consume about 35 per cent of the total cycle duration.

Tests conducted at this plant show rather conclusively that the rate of metal elimination from the slag is chiefly a function of the existing metal concentration, although indications are that the depth of slag in the furnace also exerts considerable influence. The latter factor is no doubt an

expression of the time of contact between the slag and the CO gas bubbles. Fig. 5 depicts a typical set of metal-elimination curves that were plotted from the analysis of samples of the slag heads and tails and of intermediate tuyere samples taken throughout the fuming period. In Table 2 is listed the time of sampling together with the sample analysis, slag weight, zinc weight, and elimination rate for the particular time designated. The final column lists the average zinc-elimination rate for the total time elapsed with regard to the respective samples. These data demonstrate the relationship between elimination rate and the metal concentration in the slag.

Upon completion of each fuming cycle the furnace is drained through two tapered tapholes* in the back† of the furnace. A short cast-steel launder conveys the slag through a right-angle bend to a large, concrete granulation pit‡ just north and east of the furnace. This pit is fitted with a 50-ft. wood stack for discharging accumulated vapor, also overflow and drainage outlets. The bottom is divided into five troughs sloping to large, manually operated discharge doors. A manifold below the end of the slag launder delivers water at 150 lb. pressure through ten 3/8-in. jets into the slag stream. The chilled, granulated slag is distributed throughout the chamber, settled, and decanted.

Removal of the granulated slag is accomplished by sluicing through the manually operated discharge doors, from which it is laundered to one of two 6-in. Hydroseal pumps. These pumps deliver the slag through pipe lines to a new slag dump

* Tapholes taper from 5-in. diameter on the inner jacket wall to 6 in. at the outer wall.

† For emergency, in case of power failure, two similar tapholes are provided in the front of the furnace. These two holes drain to two cast-steel launders, which convey the slag to 130-cu. ft. Treadwell pots for haulage to the slag dump.

‡ The design and general slag-granulation arrangement was supplied by the Allen-Sherman-Hoff Company.

(Fig. 2) some 920 ft. north of the fuming plant. A detailed outline of operational steps comprising Bunker Hill slag granulation and disposal practice is given in

charge hole and, when necessary, by cracking doors provided in the cross-over flue. The dust-laden gas leaves the furnace at temperatures ranging somewhat over



FIG. 2.—NEW SLAG DUMP, BUNKER HILL SMELTER.

Table 1. These data are graphically depicted in Figs. 3 and 4. Fig. 3 illustrates the relationship between the fuming furnace cycle and the slag-disposal operations. Fig. 4 shows the distribution of the total water requirement between the operational steps.

GAS TREATMENT AND DISPOSAL SYSTEM

The mixture of metal vapor and condensed oxide fume above the slag bath is carried by the flow of combustion gases venting the fuming furnace over a water-cooled bridge wall, through a water-jacketed cross-over flue into the combustion chamber of a waste-heat unit. Along the path of flow, prior to entering the boiler proper, oxidation of the metal vapor and the combustion of CO gas is completed. Air for this task* is bled in through the

2000°F. and enters the waste-heat unit from 1700° to 1900°F.

Waste-heat Unit

The waste-heat unit is a Babcock and Wilcox Co. three-drum waste-heat boiler fitted with a water-cooled combustion chamber followed by a three-drum economizer. The combustion chamber is 12 ft. square on the inside and 40 ft. high. Its sides are constructed of 3 1/4-in. o.d. tubes set on 3 3/8-in. centers to form an essentially 100 per cent black surface wall. The upper ends of the tubes enter the top drum of the boiler and the lower ends are fitted into headers that take their water supply from the boiler mud drum. The side walls are arranged to form a hopper bottom and the refractory-lined hopper is fitted with a

to deliver up to 26,200 cu. ft. per min. tertiary air at 0.75 in. H₂O through ports provided on either side of the cross-over flue. The forced entrance of tertiary air has been found unsatisfactory and unnecessary.

* Original plans called for the supply of tertiary air by means of a Sirocco, No. 8, American HS fan. This fan at 535 r.p.m. was

water-cooled screw conveyor. The front and rear walls have the tubes so spaced as to form a screened opening for the entrance of gases from the cross-over flue of the water-cooled furnace, and for the outlet of the gases to the boiler. The entire unit is housed in an insulated refractory lining fitted with a steel-plate housing and provided with suitable lance openings for cleaning and inspection.

boiler surfaces by the zinc oxide fume, the waste-heat boiler has been fitted with four tiers of small hand-lancing doors on each side.

The combined unit is rated at an output of 47,000 lb. steam per hour at 250 lb. gauge, for a feed-water temperature of 220°F. The heating surface consists of: combustion chamber, 2174 sq. ft.; boiler, 7723 sq. ft.; economizer, 4757 sq. ft.

TABLE 1.—*Slag-disposal Operations, March 1944*
Tapping Interval, 110 Minutes. Slag Tapped, 30 Tons.

Operation	Time, Min.	Water Consumed, Gal.	Procedure
Granulation.....	6	6,000	Water at a rate of 750 gal. per min. is delivered at 150 lb. pressure to ten $\frac{3}{8}$ -in. jets. Tapping requires 6 min. but pump is running about 8 min. Pump is 6-in., 75-hp. Hydroseal
Decantation.....	15		Slag in granulation pit is decanted by means of two 6-in. 1000-gal per min. Hydroseal pumps. This water is delivered to slag dump through two 920-ft., 6-in. dia., mild-steel pipe lines. Standard threaded pipe joined by sleeve couplings is used. The pit is not completely drained before the sluicing operation is started
Sluicing..... (Granulated slag = 2 % + 4 mesh 100 % + 65 mesh)	45	44,600	Starting on side close to pumps, slag-discharge doors are progressively open and slag sluiced to a 30-in. wide by 18-in. deep Ascolite launder. Each of five discharge doors is provided with a 175-gal. per min. oscillating sluice jet. No more than two jets are in operation at a time Ascolite launder that conveys slag to pump sump is provided with two sluicing jets—one 225-gal per min. at end of launder away from pump and one 175 gal. per min. midway. The 6-in. Hydroseal pump utilized for granulation supplies these sluicing jets at 150 lb. pressure as well as a 150-gal. per min. pump sump agitator. One of two pump and line installations (described above under "decantation") is used for the delivery of granulated slag to the dump. At 38 lb. pumping pressure, 1000 gal. per min. at 15 per cent slag by weight is delivered 920 ft. to slag dump (75 hp., 830 r.p.m.). From pump level pipe lines rise 13 ft. 8 in. in 320-ft. distance. Remaining 600 ft. is down grade, the discharge point being 5 ft. 4 in. below pump elevation. At the highest point of line elevation a 70-ft. high standpipe is installed. Pump volume is maintained at 1000 gal. per min. by a float valve in the pump sump
Filling granulating pit	13	30,600	After slag-discharge doors are closed, a valve on a 10-in. line from water reservoir is opened and 30,600 gal. drawn into pit.
Total.....	79	81,200	

Pipe line: { Straight line runs, no noticeable wear after eight months.
90° sweeping bends, apparent life will approach 1 to 2 years.
Threaded pipe ends within couplings, apparent life, 10 months. Heavy erosion for a few inches on both ends within sleeve coupling. This possibly may be avoided by butting pipe lengths together within coupling.

Boiler and economizer tubes are $2\frac{1}{2}$ in. o.d. except for some 4-in. o.d. downcomer tubes. All these tubes are essentially vertical, to permit ready cleaning, and discharge to hoppers that extend the full length of the unit under the lower drums. To combat a severe fouling action of the

Auxiliary oil burners of a size to permit the generation of steam up to 15,000 lb. per hour are also provided in the waste-heat combustion chamber.

For emergency, an auxiliary boiler of the Babcock and Wilcox integral furnace type, fired with pulverized coal is also installed

as a standby. This boiler has a heating surface of 3127 sq. ft. plus a water-wall surface of 500 sq. ft. The unit is rated at 24,000 lb. steam per hour from feed water

use of an internal water-treatment system. Daily analyses of boiler-water samples determine both the quantity of corrective agents* required and the volume of con-

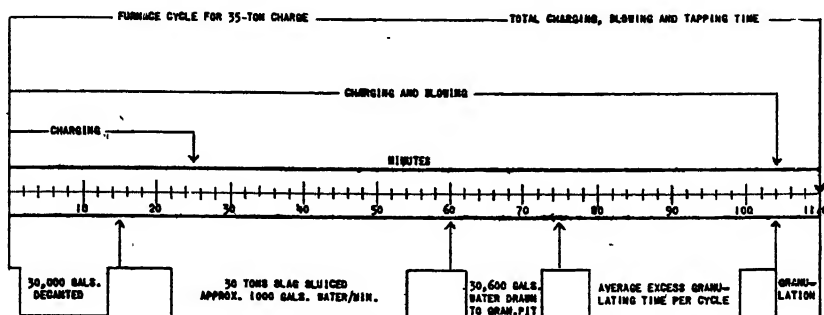


FIG. 3.—SCHEDULE OF FUMING-FURNACE AND SLAG-DISPOSAL CYCLE, MARCH 1944.
13 cycles per day; 35+ tons per cycle.

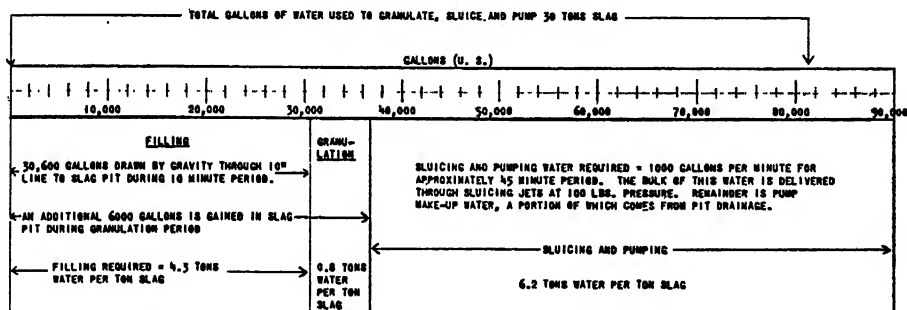


FIG. 4.—WATER REQUIREMENTS FOR SLAG GRANULATION AND DISPOSAL.
Reservoir storage capacity, 260,000 gallons.

at 220°F. to steam pressure of 250 lb. gauge. Both the auxiliary and waste-heat units were originally fitted with automatic soot blowers supplied by the Northern Equipment Co., Copes feed-water regulators, and Reliance high and low-water alarm water columns. While the automatic soot blowers are still used in the economizer section, those installed in the waste-heat boiler did not stand up under the combined heat and fluxing action to which they were subjected. All cleaning of the waste-heat boiler is manual. Steam-air hand lancing every cycle is practiced.

About 70 per cent make-up water, supplied from the smelter domestic water system, is consumed in boiler operation. The character of this water permits the

tinuous boiler blow-down necessary. Incoming feed water is delivered by pump, through a Cochrane deareator, to an insulated steel hot-water storage tank.

In passage through the waste-heat unit the dust-gas temperature is decreased from about 1800°F. at the combustion chamber inlet to an average of about 700°F. at the economizer outlet; intermediate temperatures approach 1500°F. at the boiler inlet and 900°F. at the economizer inlet. The steam generated through the heat transfer obtained is ample to

* The internal water-treatment equipment, specifications and reagents are supplied by the Flox Company, Inc. Small reagent feeders permit the solution and continuous addition of two corrective agents, No. 7AF for oxygen removal and No. 747 for softening.

supply the requirements of the Sullivan Mining Co. zinc plant and the Bunker Hill mine, as well as for general smelter usage, which, as already stated, includes the driving of blowers, boiler feed-water pumps and the stack fan within the slag-treatment plant.

Flue System and Baghouse

The 700°F. outlet gas from the economizer is drawn through a rectangular, steel downtake flue, which connects with a 168-ft. span of 10-ft. balloon flue, before entering a bank of cooling towers. Here the gas flow, at about 575°F., is split into four parallel streams, each passing through five 38-in. diameter by 60-ft. high inverted U-tubes arranged in series. Beneath the towers the dust cellar is divided into six hoppers compartments that are screw-discharged at right angles to the gas flow. The combined cooling-tower outlet gas, at approximately 250°F., is distributed from a 96-ft. length of 10-ft. balloon flue into five 50-ft. Northern Blower automatic baghouse units. The five parallel baghouse units comprise 10 sections, each section containing 78 bags that are each 6 in. in diameter by 8 ft. long. The bags are automatically shaken into cellars hoppers to common discharge screws. Adjustable timers enable ready changes in the shaking frequency to accommodate variable baghouse conditions. The baghouse inlet temperature is maintained at about 200°F.; automatically operated louvers, installed after the cooling towers, provide the admission of cooling air when necessary.

Fan and Gas-disposal System

For gas transportation and disposal, other fuming-plant installations have employed multiple fan systems, one or more of the fans being installed ahead of the baghouse exposed to the dust load. To avoid the difficulties resulting from the build-up of dust accretions on the fan housings and impellers, the Bunker Hill

plant utilizes a single fan installed after the baghouse at the base of a 200-ft. brick stack. The entire gas flow is motivated by a size 10½ Sirocco blower, driven by a Worthington-Moore turbine of 270 hp. at 225 lb. gauge pressure and 27 in. Hg vacuum. The range of blower operation obtainable is as follows:

	Minimum	Maximum
Gas temperature at 200°F., volume, cu. ft. per min....	25,000	125,000
Blower, r.p.m.....	112	557
Inches water static pressure.....	0.45	10
Boiler hp.....	4	270

Dust Collection and Disposal

With the exception of the cross-over flue, the dust from the entire gas system is mechanically discharged as produced, and continuously conveyed to a deleading kiln, through an intermediate, 300-ton dust-storage bin. A belt conveyor parallels the gas flow beneath the waste-heat unit, flues, cooling towers and baghouse. Like the hoppers of the waste-heat unit, cooling towers and baghouse, the connecting flues are continuously screw-discharged. Nine-inch ribbon screws, operating in troughs fitted into the hoppers of the balloon sections, discharge their dust load through counterweighted gates into rectangular steel chutes to the belt conveyor below.

An eastward-moving belt collects and transports the screw discharges from the combustion chamber, boiler, economizer, and from about one half of the balloon flue span connecting with the cooling towers. Two westward-moving belt systems gather the residual dust load. One of these belt systems collects the load from the cooling towers and remaining flue discharge units; the other serves the baghouse. All three of the belt systems spill their respective loads onto a common cross conveyor, which moves north to a bucket elevator. The electrical drives of both the screw and belt conveyors are interlocked so as to

circumvent spills and overloads. The stoppage of any common conveyor automatically cuts out all screws and belts that serve it.

The bucket elevator, receiving the combined dust load, discharges into a multiple-outlet screw conveyor; which spans the length of a rectangular concrete storage bin 60 ft. long by 13 ft. wide by 15 ft. deep. Four parallel ribbons in the bottom of this bin discharge the dust load to a common screw operating at right angles. The dust flow then proceeds to the deleading kiln through a volumetric measuring hopper and a second bucket elevator.

DENSIFICATION AND DELEADING

At East Helena, Mont., and at Trail, B.C., the slag fume is shipped directly, as collected, to the electrolytic plants for reduction to zinc metal. The local Sullivan Mining Co. electrolytic zinc plant, owned jointly by the Bunker Hill and Sullivan Mining and Concentrating Co. and the Hecla Mining Co., is operating at capacity on zinc concentrates. Expansion of the present electrolytic zinc plant to handle this increased tonnage and the establishment of new operating procedures to accommodate the treatment of slag fume, which contains small quantities of elements such as fluorine and chlorine, detrimental to electrolytic zinc processes, would consume considerable vital time and material. Therefore, to expedite the delivery of much needed zinc to market it was decided to ship the zinc oxide, at least temporarily, to a retort plant.

The composite fume collected from slag-treatment operations averages about 63 per cent Zn, 10 per cent Pb, and weighs approximately 40 lb. per cu. ft. For reduction to metal at a retort plant, it is necessary that this product be densified and its lead content greatly reduced. These requirements are accomplished by heat-treatment in a rotating kiln* with about

1.5 per cent, by weight, of minus $\frac{1}{4}$ -in. crushed coke.

The bucket elevator, receiving the material from the zinc-dust intermediate storage bin, discharges to a pug mill, which also receives the crushed coke. Delivery of the mixed pug-mill product into the rotating kiln is accomplished by means of a water-cooled screw operating at a steep angle. The kiln proper slopes from a brick settling chamber at the feed end—at a rate of $\frac{1}{2}$ in. per foot—to the combustion hood at the discharge end. The kiln is 75 ft. long by 7 ft. diameter; is lined with 6 in. of firebrick and rotates at a rate of 1.0 r.p.m. An auxiliary diesel electric unit of adequate capacity to drive the heated kiln in the event of a power failure is provided. The kiln is oil-fired countercurrent to the charge flow. At the present time manual regulation of the kiln temperature is practiced. However, the installation of a Bailey oil-air ratio controller and automatic temperature controller for closer regulation of kiln firing is in progress.

In its passage through the kiln the charge is densified and delead by exposure to temperatures grading from about 1100°F. at the feed end to 2350° to 2500°F. at the discharge end. The kiln feed weighs about 40 lb. per cu. ft. and contains around 10 per cent Pb. The kiln discharge weighs about 185 lb. per cu. ft. and averages about 3.5 per cent Pb. From the rotating kiln the hot, densified discharge drops through the combustion hood, over a 4-in. grizzly, into a circular cast-iron chute, from which it is distributed into a rotating, six-tube cooler.* The water-sprayed cooler slopes to a discharge hopper delivering the cooled charge onto a belt conveyor for transportation up an incline to a concrete storage bin for zinc oxide. From this bin the oxide product, at about 72 per cent Zn, is pulled

the fluorine and chlorine are also eliminated in the kiln treatment.

* Both the kiln and discharge-cooler installation were supplied by the Traylor Engineering and Manufacturing Co.

* It has been found that practically all of

through two manually operated gate-and-chute arrangements into railroad cars for shipment.

The lead fume, venting the kiln at the feed end, is drawn to a set of cooling towers through a brick settling chamber and a span of 8-ft. balloon flue. In the cooling towers the flow is split between four parallel sets of 38-in. dia., 60-ft. inverted U-tubes, two inverted U-tubes comprising the series in each set. The cooling-tower outlet is connected to a single 20-ft. Northern Blower automatic baghouse unit by 40-in. circular flue through a right-angle bend. Short sections of this circular flue enter a rectangular box arrangement at right angles. The intermediate box is fitted with automatically controlled louvers for the intake of cooling air when necessary.

The lead baghouse contains four sections, each containing 78 bags, 6 in. diameter by 8 ft. long. Adjustable timers, as in the larger ZnO units, control the operation frequency of the bag-shaking mechanism. The clean discharge gas is removed and vented by the same fan and stack serving the slag-fuming operation.

Continuous removal and transportation of the dust from the combustion chamber, flues, cooling towers, and baghouse is practiced as described for the slag-treatment system. The dust collected as far along as the cooling towers is high in zinc and is circulated back to join the kiln feed. The lead baghouse fume, at about 50 per cent Pb and 23 per cent Zn, is transported up an inclined belt conveyor to a hoppers, steel storage bin. From this bin it is discharged into cars and returned to the lead-smelting system through the Dwight-Lloyd roasters.

OPERATING CONTROL

To facilitate the operation of the slag-treatment plant, a very efficient and informative control system was designed by the Bailey Meter Co., of Cleveland,

Ohio. A control panel, 8½ ft. high by 15-ft. long, is installed close to the fuming furnace in a room housed against plant dust. From this control board the operator has visual information concerning practically all important factors pertaining to the operation of fuming furnace, boilers, baghouses and deleading kiln. Nine recording meters mounted at eye level continuously record temperature and draft conditions, air flow, steam flow and steam pressure. At the top of the board are signal lights and multipoint gauges giving visual indications of the existing pulverizer, blower, flue, and baghouse conditions. Between the recording meters and the multipoint indicators are mounted ammeters relating the power input to the four pulverizers, and gauges showing the air-line pressures at the blower discharge and at the pulverizer inlets. On the lower half of the panel are installed pulverizer feeder and fuel-air ratio controls, starting switches, and selector valves. By means of the selector valves, plant conditions may be adjusted. Set operating conditions may be either automatically maintained or manually controlled.

PLANT OPERATION AND METALLURGY

Starting Operations

As stated early in the paper, operation of the slag-treatment plant commenced on April 5, 1943. Initial operations were unusually successful.* Within the designed operating range, ample furnace draft, gas cooling and baghouse capacity were in evidence. All auxiliary equipment, and

* Much credit is due to the fine cooperative service rendered by the Anaconda Copper Mining Co. at East Helena, Mont., and the various equipment manufacturers through their service engineers. During the first few weeks the fuming furnace was operated under the capable supervision of R. L. Thompson, Assistant Superintendent, and Tom Sitton, General Foreman, of the slag-treatment plant at East Helena. In boiler and pulverizer operations invaluable assistance was provided by the Babcock and Wilcox engineers, M. S. Gerend, E. R. Stahl, and A. L. Jordan. Similar helpful cooperation was obtained from Ray Harper, of the Ingersoll-Rand Co., and H. T. Sawyer, of the Bailey Meter Company.

particularly the direct pulverized-coal-firing system, functioned very satisfactorily. The first few exploratory runs, wherein low coal flows and excess air were employed as a precaution against the freezing of the furnace bath, were characterized by relatively poor elimination of zinc. By the fourth charge, however, conditions were adjusted to produce a furnace tailing slag assaying 0.5 per cent zinc. In all subsequent furnace operations the discharge slag has been consistently maintained at about 1.0 per cent zinc for 300 tons per day and about 1.9 per cent zinc for 450 tons per day.

TABLE 3.—*Plant Conditions Existing during Run 221-7. Furnace Charge 455*

Slag charge, tons.....	34.6
Cycle, min.: { Charging, 32 Blowing, 102 Tapping, 10 }.....	144
Treatment rate, 10 cycles per day, 346 tons hot slag per day	
Zinc:	
Content of slag heads, lb.....	10,910
Content of slag tails, lb.....	770
Eliminated during cycle, lb.....	10,140
Eliminated per minute, lb.....	70.3
Quantity eliminated, per cent.....	92.8
Coal consumed, lb.:	
During cycle.....	14,500
Per lb. zinc eliminated.....	1.45
Steam generated, lb.:	
Per hour @ 240-lb. gauge.....	36,300
Per pound coal.....	6.0
Average air volume to tuyeres, cu. ft. per min.:	
Primary.....	3,850
Secondary.....	4,900
Total.....	8,750
Average gas analysis at economizer out- let, per cent:	
CO ₂	10.4
O ₂	8.0
CO.....	0.0
N ₂	81.6
Baghouse drafts cond., in. water:	
Inlet.....	2.5
Outlet.....	3.5
Differential.....	1.0

The chief difficulty attending the starting operations concerned the system installed for the transfer of ZnO dust from the slag-treatment unit to the deleading kiln. The oxide dust particles displayed a marked tendency to intermesh and hang up at any point in the flow where area restrictions more or less subjected the dust to compression. Original plant design called for the transfer of the zinc oxide dust to the deleading kiln through a relatively small, conical shaped, surge hopper. This

intermediate hopper was fed by bucket elevator and discharged through a Merchen scale feeder. The dust proportioned by the Merchen feeder was to be conveyed to a second bucket elevator for delivery to the kiln. This transfer arrangement proved a continual source of trouble. Frequent plugging of the elevators occurred in the restricted areas of the feed hoppers and discharge chutes. It was also soon apparent that the proportioning of deleading kiln feed from the conical surge hopper was impractical. Continuous, wide fluctuations in the bin-discharge rate accompanied successive arching and flooding actions. The dust readily arched in the constricted hopper outlet and all attempts and devices either to break the arch or to prevent its formation caused flooding.

Elevator difficulties have been corrected by elimination of the area restrictions in the intake hoppers and discharge chutes. The troublesome conical surge hopper has been replaced by a large rectangular storage bin, described in the foregoing section on Dust Collection and Disposal. The use of this large storage bin has provided a comfortable margin in the plant gas-cooling capacity. Prior to its installation, owing to the lack of adequate dust storage, heavy loads were carried a good part of the time in the hoppers subtending the flue, cooling tower and baghouse system. Present operation, with practically no load in these hoppers, enables the usage of considerable additional cooling surface.

A second difficulty, thought to be closely related to the dust-transfer and storage problem, still persists to a lesser degree; that is the operation of the deleading kiln. Elimination of lead is erratic and there is an excessive build-up of wall accretions. Before the installation of the large bedding and storage bin, the kiln feed was very irregular, both as to quantity and character. The feed was delivered, more or less, as produced from the collection belts that parallel the entire dust system. With

the introduction of the bedding, mixing, and storage facilities provided by the new surge bin, greater improvement in kiln operation than that experienced to date was anticipated. As already related, closer regulation of the kiln temperature is now being effected by the installation of temperature and oil-air ratio controllers. The function of the small percentages of coke added as an aid to elimination of lead is obscure. Efforts are in progress for the development of some substitute agent, preferably one that will permit kiln operation in a lower temperature range.

Routine Plant Operation

Over the 15-month plant life to date, operation has been maintained 93.37 per cent of the total elapsed time. Distribution of the 6.63 per cent lost time is as follows:

CAUSE	LOST TIME, PER CENT
Changing tuyeres and pipes	1.68
Rebrickng deleading kiln..	1.87
Washing jackets.....	0.78
Blast furnace down.....	0.72
Fuming-furnace repair....	0.66
Boiler repair.....	0.59
Pulverizer repair.....	0.09
Fire in air header.....	0.20
Power failure.....	0.04
Total to date.....	6.63

This percentage of lost time should be fairly representative of average plant operation in the future. The causes listed are well distributed throughout the various phases of the plant operation.

The operating crew per 8-hr. shift consists of: 1 shift boss, 1 furnace operator, 2 furnace helpers, 1 granulation man, 1 boiler operator, 3 boiler lancers, 1 tower man, 1 baghouse operator, 1 kiln operator, 2 kiln helpers, 1 coal operator.

Plant Capacity and Metallurgy

As mentioned, the plant capacity over the first six months operation averaged under 300 tons per day. Only 15 per cent

of the charge was reclaimed dump slag; the other 85 per cent represented all current slag produced in the smelting of incoming ores. However, while awaiting preparations for the smelting of increased tonnages of dump slag, larger charges were treated on several occasions. These trial runs indicated that the maximum capacity of the existing plant installation approached 450 tons of hot slag per day. The metallurgical data describing two of these trial operations are presented by the accompanying tables and graphs.

The metal elimination rates depicted by Table 2 and Fig. 5 represent plant operation on a basis of 346 tons of hot slag per day. Other pertinent plant conditions prevailing at this treatment rate are listed in Table 3. A similar group of data showing metal elimination rates and plant conditions when operating at maximum capacity are depicted by run 221-8, charge No. 520. Table 4 lists the data employed for the plotting of the metal-elimination curves of Fig. 6. General plant conditions existing during this run are presented by Table 5.

In run 221-7 (Table 2), $\frac{14,500}{144} = 101$ lb. of coal per min. and 8750 cu. ft. per min. of total air were supplied to the furnace tuyeres. An attempt was made in the subsequent test, 221-8, Table 4, to deliver the same total coal and air, as above, in a 120-min. interval, or 121 lb. coal per min. and 10,300 cu. ft. per min. air. However, a very high furnace-outlet draft was required to overcome the surging of fume to atmosphere through the furnace charge hole; also, the steam generated exceeded the boiler capacity. After a short interval of operation, it became necessary to reduce the coal flow to 112 lb. per min. and the total air volume to 9640 cu. ft. per min. Subsequent high-capacity test runs indicated that the excessive surging of fume through the furnace throat was due to a bad fouling of the flue system at the entrance to the boiler. Upon the provision

of additional lancing ports at the boiler plant capacity approaching 450 tons of inlet, run 221-9 was completed without hot slag per day was practical.

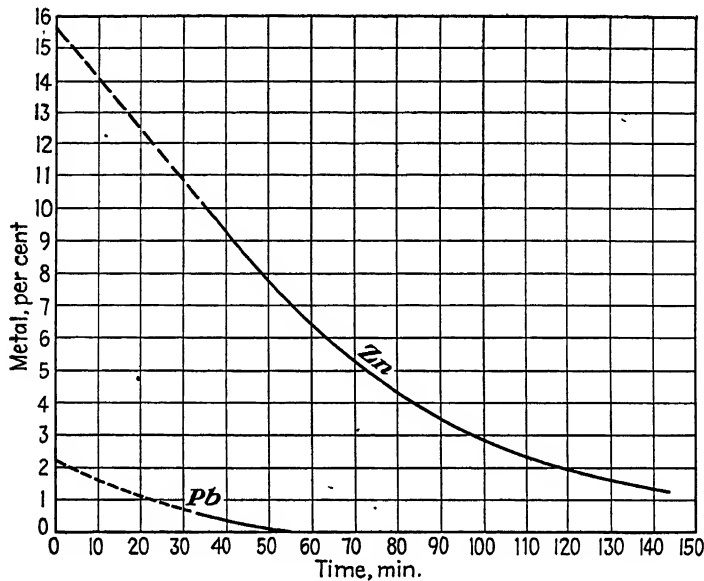


FIG. 5.—METAL-ELIMINATION TESTS, RUN 221-7. FURNACE CHARGE 455.

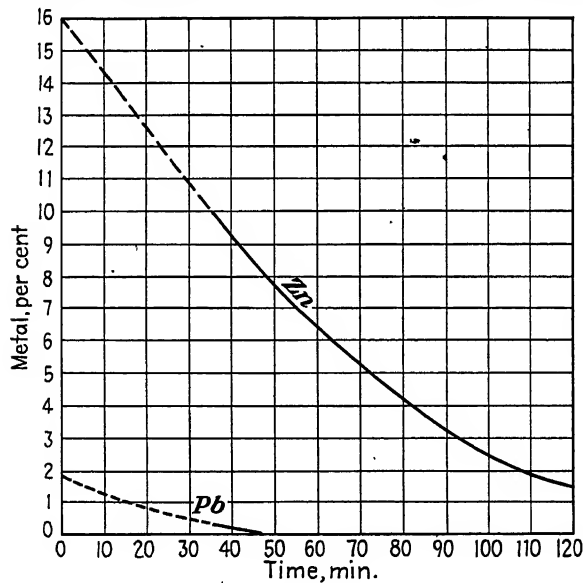


FIG. 6.—METAL-ELIMINATION TESTS, RUN 221-8. FURNACE CHARGE 520.

incident at atmospheric air temperature ranging between 87° and 89°F. This run, summarized in Table 6, indicated that a Routine plant operation over the last nine-month interval substantiates these tests. Several monthly averages of 450

tons per operating day have been recorded. Owing to the low elevation of the charge spout, 35-ton charges have been found preferable, thirteen 110-min. cycles being employed. The furnace cycle now averages: charging time, 27 min.; blowing time, 77 min.; tapping time, 6 min.; total, 110 minutes.

TABLE 5.—*Plant Conditions during Run 221-8. Furnace Charge 520*

Slag charge, tons.....	37.6
Cycle, min.: { Charging, 27 Blowing, 83 Tapping, 10 }	120
Treatment rate, 12 cycles per day, 451 tons hot slag per day	
Zinc:	
Content of slag heads, lb.....	12,040
Content of slag tails, lb.....	777
Eliminated during cycle, lb.....	11,263
Eliminated per minute, lb.....	93.9
Quantity eliminated, per cent.....	93.5
Coal consumed, lb.:	
During cycle.....	13,450
Per lb. zinc eliminated.....	1.19
Steam generated, lb.:	
Per hour @ 250 lb. gauge.....	43,750
Per lb. coal.....	7.8
Average air volume to tuyeres, cu. ft. per min.:	
Primary.....	4,260
Secondary.....	5,380
Total.....	9,640
Average gas analysis at economizer outlet, per cent:	
CO ₂	13.1
O ₂	5.4
CO.....	0.1
N ₂	81.4
Baghouse draft cond., in. water:	
Inlet.....	2.5
Outlet.....	3.7
Differential.....	1.2

TABLE 6.—*Average Fuming-plant Data during Furnace-capacity Test 221-9, Furnace Charge 866, July 20, 1943*

Slag charge, tons.....	37.4
Cycle, min.: { Charging, 29 Blowing, 81 Tapping, 10 }	120
Treatment rate, 12 cycles per day, 449 tons slag per day	
Zinc:	
Content slag heads, lb.....	10,567
Content slag tails, lb.....	923
Eliminated during cycle, lb.....	9,644
Eliminated per minute, lb.....	80.4
Quantity eliminated, per cent.....	91.3
Coal consumed lb.:	
During cycle.....	13,800
Per lb. zinc eliminated.....	1.43
Steam generated, lb.:	
Per hour @ 250 lb. gauge.....	45,250
Per lb. coal consumed.....	6.55
Air volume to tuyeres, cu. ft. per min.:	
Primary.....	4,400
Secondary.....	4,500
Total.....	8,900
Baghouse outlet draft, in. water.....	3.9

Slag tailings average 1.9 per cent zinc, about 0.4 per cent higher than indicated in the test runs. Probably this is due to a decrease in the depth of the slag bath and to the practice of adding about 15 per cent of the charge weight as cold slag to maintain high-tonnage operation. The total dump slag processed now approximates 65 per cent of the furnace charge as compared with a total of 15 per cent in early operations. Current steam production somewhat exceeds the rated waste-heat boiler capacity. In that the waste-heat unit comprises the limiting factor, future increases in capacity will depend upon more efficient reduction of metal. This may possibly be effected by raising the furnace charge spout so as to permit the treatment of larger charges of additional bath depth.

ACKNOWLEDGMENTS

For plant design and construction the writers wish to acknowledge the capable work of the Bunker Hill and Sullivan engineering staff, under the supervision of A. D. Moir, chief engineer.

Of particular value in both preparatory stages and in actual plant operation was the generous provision of drawings and available information by the staffs of: The Anaconda Copper Mining Co., East Helena, Mont.; The Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B.C.; The International Smelting and Refining Co., Tooele, Utah.

The very satisfactory performance of the slag-granulation system is largely due to the able supervision of initial operations by P. L. Alexander, of the Allen-Sherman-Hoff Company.

In the determination and assembly of metallurgical data, much assistance was provided by Donald Ingvaldstad and Farrel Alsop, of the Smelter research staff.

Deaeration in Manufacture of Zinc Retorts

By M. M. NEALE,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE pottery department has been aptly described as the "heart of the zinc plant," and every operator of a horizontal-retort plant is acquainted with the fact that good retort practice is the keystone of the smelting process. Since retorts and condensers are clay products, it is obvious that improvements in other branches of the ceramic industry should be observed for possible adoption in the pottery process for zinc smelting.

Deaeration of clay bodies is one of the improvements that have become fully established in many brick and pottery plants. Our investigation of a number of these installations always yielded the same answer—improved practice. Improvement in workability, elimination of laminations, less porosity, greater wet and dry strength, were among the claims put forth for this process. All of these features are exceedingly desirable characteristics in the manufacture of a zinc retort.

A preliminary test, which involved truck transportation of deaired slugs over a relatively long distance, did show the value of many of these characteristics in forming the retort. Results from the standpoint of longer retort life in the smelting furnace were not outstanding.

The idea lay dormant for several years but was revived again in 1940, when it was decided to make whatever changes were necessary in the equipment for pottery manufacture to fully demonstrate the process. A number of the manu-

facturers of machinery for clay work were asked to submit proposals, and the plan finally adopted was extremely simple and economical.

MACHINE FOR DEAERATING CLAY

Selection of the "straight-line" principle for conversion of the "Wettengel" pug mill to a "vacuum-extrusion" machine preserved some usable parts of the original equipment, such as the drive mechanism and main shaft. The converted machine consists of a feed hopper, a compression and shredding zone, a vacuum chamber, and an extrusion barrel, as shown in Fig. 1.

In operation the clay mix travels from the feed hopper into the compression zone, where it is compressed and finally forced around the tapered cone into the vacuum chamber. As it enters this chamber the clay body is shredded into thin plates, for exposure to the vacuum. The shredder consists of a hub mounted on the main shaft, to which are bolted segmental sections, each of which carries shredder knives. The compression zone and extrusion barrel function as seals for the vacuum chamber and the shredded clay mix is agitated thoroughly during its exposure to the vacuum. A vacuum pump, equipped with a 3-hp. motor, is attached to this chamber, and maintains 25 to 26 in. vacuum during operation of the mill.

CHANGES IN PRACTICE

Prior to the adoption of the deaeration process, our standard pottery practice called for double mixing in the combination

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machine before storage in the "rot room." The first change in practice was to eliminate this extra mixing, although the practice of "rotting" is still followed, principally as

As far as costs are concerned, the power requirements for the vacuum pump are less than for the extra mixing under the old practice and maintenance expenses

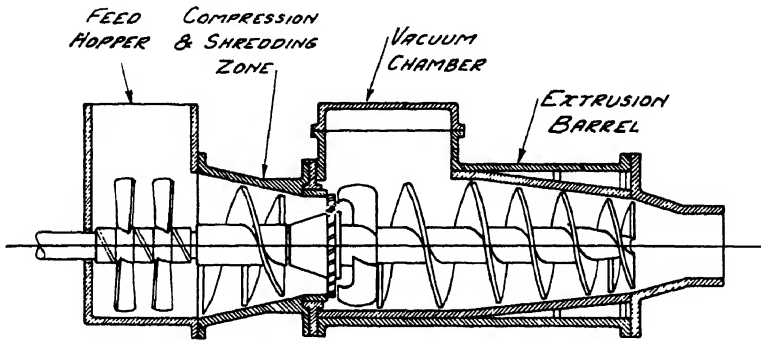


FIG. 1.—VACUUM-EXTRUSION MACHINE FOR DEAERATING CLAY.

a storage convenience. The fine shredding of the clay mix for exposure to the vacuum yields better results than double mixing and also permits greater latitude in the moisture content without detrimental effects to the retort body. Other advantages that have accrued from the deaeration process are improved strength, straightness, and a marked decrease in dry-room scrap from warpage and cracks.

The improvement in strength is demonstrated by rupture tests, the following figures representing an average of a series of tests with the same clay mix:

Clay Mix	Modulus of Rupture, Lb. per Sq. In.	
	Dry	Fired
Nondeaired.....	271	1205
Deaired.....	350	1731

The denser body produced by the vacuum process permits the use of higher temperatures in the early stages in the dry room as well as an accelerated rate of temperature increase during the actual drying period, so that over-all drying time can be reduced about 25 per cent.

remains about the same as before. It is evident that the other gains in manufacturing practice and costs with the deaeration process have been able to show a very satisfactory return on the capital investment.

IMPROVEMENTS IN PRODUCT

In the zinc furnace department the increased dry strength has been extremely advantageous in the transportation, handling, and loading of retorts into the preheating kilns. Rejections for spalling and fire cracks at the kilns have been reduced almost to the vanishing point. In the zinc furnace itself retort life has been increased approximately 17 per cent as compared with the average for a two-year period prior to deaeration. Moreover, these results have been achieved under labor conditions far more difficult than those existing in 1939 and 1940. The deaeration process has been so uniformly successful that there is no discernible variation in the quality of the individual retorts, and one more variable in the smelting process has become a constant, for all practical purposes.

Another possible advantage in the deaeration process lies in the replacement

of Missouri clay—a very pertinent subject at this time. To date we have only partly explored this field, but have succeeded in replacing up to 30 per cent of the Missouri clay with that from another source. It is our opinion that part of the success in this direction is due directly to the uniformity of the mix in the deaeration process.

As soon as the operating practice from this change in retort manufacture was firmly established, the information was passed along to other plants making horizontal retorts for zinc smelting. At the present time four or five plants have adopted deaeration and we believe they are obtaining results comparable with those claimed for the Donora Zinc Works.

Pneumatic Conveying at Giesche Spolka Akcyjna, Poland

By ROY E. THOMAS,* MEMBER A.I.M.E.

(New York Meeting, February, 1939)

Soon after the Waelz plant for the fire concentration of low-grade zinc ores was put into operation in the early part of 1929 at Katowice, it was found that the conveyor equipment for transporting the hot residue from the furnace dust chambers was inadequate. Hand tramming with water cooling was used for a time, but that method was injurious to the workmen as well as costly. The problem was to find some practical mechanical means of conveying flue dust at temperatures of from 450° to 600°C. as it was drawn from the dust chambers. After considerable preliminary investigation it was decided to install pneumatic equipment for conveying the hot materials to a central mixing plant, where it would be mixed with slime and from which it would be returned to the furnace feed hoppers.

The first pneumatic equipment was installed in 1930, and has been in successful operation since that time. The pneumatic method of transportation has shown a considerable saving in operating costs over the former methods of dust handling and a decided improvement in working and hygienic conditions at the plant, through the elimination of the dust hazard.

Additional pneumatic equipment was installed in 1933 for conveying the furnace fume from the baghouses to the roaster plant. At the same time pick-up lines were provided for collecting the cleanings from the vertical and horizontal cooling pipes that are between the furnace dust chambers and the baghouses. The latter installation has practically eliminated a dusty and costly hand-tramming operation.

A third extension was made to the pneumatic system in 1938 for conveying the zinc-lead-cadmium fume from the roaster-plant baghouses and flues to a new re-treatment plant for secondary products.

The success of pneumatic conveying at the Waelz plant was the determining factor in the decision to install another pneumatic unit at the Saeger zinc-roasting and sintering plant. The new unit at Saeger was installed early in 1938 for the transportation of flue and Cottrell dust, small amounts of flotation concentrates to the sinter machines, and

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* Chief Engineer, Giesche Spółka Akcyjna, Katowice, Poland.

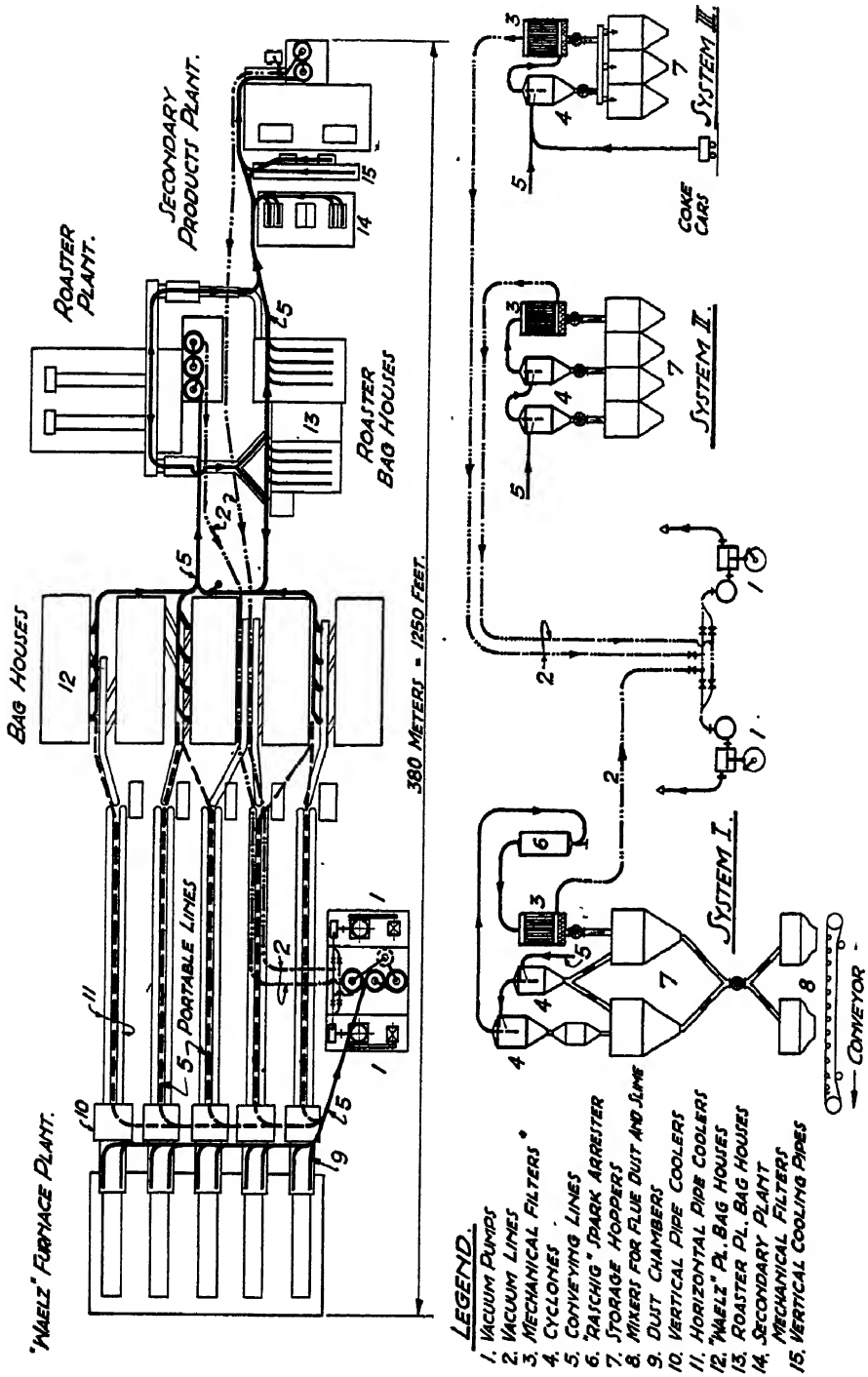


FIG. 1.—PNEUMATIC CONVEYING SYSTEMS, ZINC OXIDE PLANT.

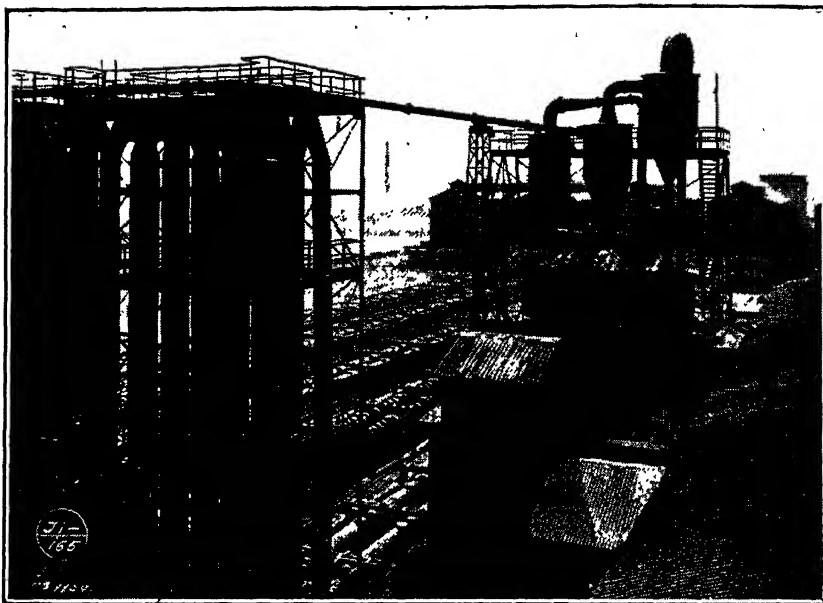


FIG. 2.—CYCLONE AND FILTER INSTALLATION FOR PNEUMATIC CONVEYING SYSTEM No. 1, ZINC OXIDE PLANT.

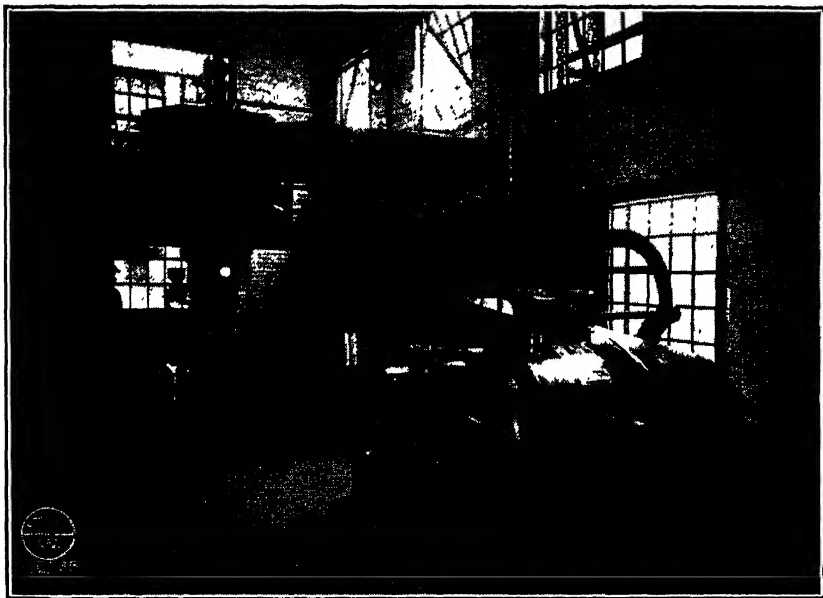


FIG. 3.—VACUUM PUMP, ZINC OXIDE PLANT.

slack coal. Connections have been provided for general clean-up purposes about the plant.

EQUIPMENT

The diagrams in Figs. 1 and 4 show the two installations at the Giesche plants; i.e., Waelz plant and Saeger roasting and sintering

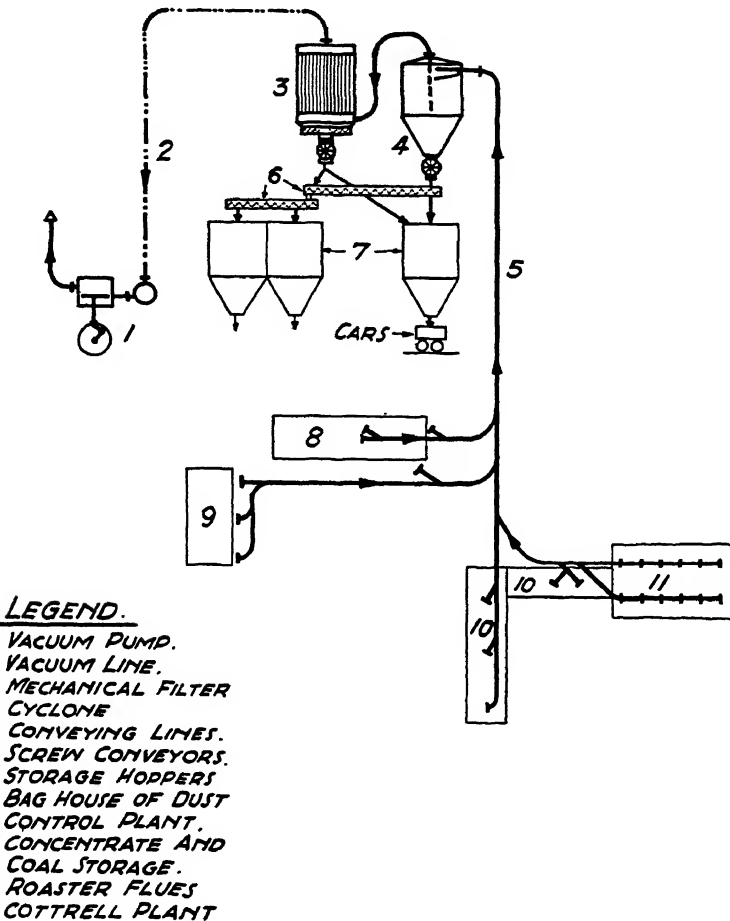


FIG. 4.—PNEUMATIC CONVEYING SYSTEM, SAEGER ROASTING AND SINTERING PLANT.

plant. The photographs (Figs. 2, 3, 5 and 6) show additional details of the equipment.

Vacuum Pumps

The pumps installed at the Giesche plants are illustrated in Fig. 7. They are of the double-acting piston type with automatic spring-actuated inlet and exhaust valves. By automatic is meant that the valves are not

positively operated by a mechanical valve gear. They are situated in a divided annular ring chamber surrounding the cylinder and cast integral with it. The valve disks are made either of leather riveted to steel disks, or of pressed fiber. Fiber disks are now used exclusively at the Giesche plants because of the deterioration of leather when conveying hot materials.

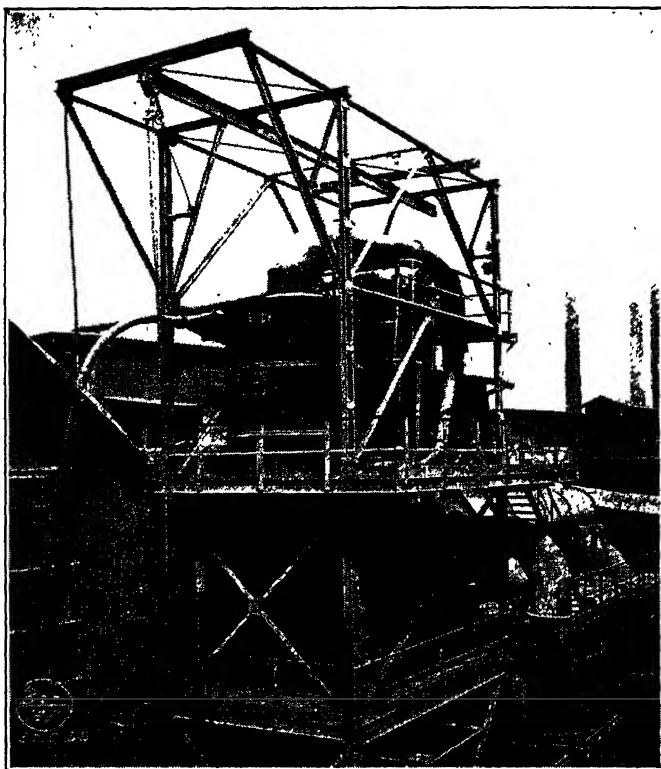


FIG. 5.—CYCLONE AND FILTER INSTALLATION FOR PNEUMATIC CONVEYING SYSTEM OF SAEGER PLANT.

The pistons are of hollow cast-iron cylindrical disk construction without piston rings. They are fitted with clearances of from 0.2 to 0.3 mm., depending upon the size of the pumps.

The piston and piston rod are centered by means of an upper cross head and a lower sliding shoe. Laminated shims are provided for adjustment. There are piston-rod packing glands in both the upper and lower cylinder heads. Asbestos packing impregnated with talcum powder has been found satisfactory.

The pumps are equipped with air receivers on the inlet sides. The air receivers are fitted with manually operated by-pass air-inlet gates for starting the pumps, and with adjustable spring-actuated vacuum valves

to prevent damage to the systems in case of plugged lines. The vacuum valves can be set to maintain the desired vacuum at the pumps.

Either open belts or short center V-belts may be used for driving the pumps. Occasionally gear and pinion drives are installed. The pumps cannot be direct-connected to the driving motors because of their relatively low speeds.

The two pumps at the Giesche oxide plant have been in operation since 1930 and 1937, respectively, with only minor repairs and adjustments. No essential pump parts have been replaced because of wear.

A number of European firms manufacture vacuum pumps of the type described. The designs vary slightly, but all are essentially of the same general construction. The pumps used at the Giesche plants were delivered by a German manufacturer. Specifications are given in Table 1.

TABLE 1.—*Pump Specifications*

Data	Zinc Oxide Plant	Roasting and Sintering Plant
Number installed.....	2	1
Cylinder diameter, mm.....	1150	770
Theoretical displacement at atmospheric pressure, cu. m. per min.....	134	52
Stroke, mm.....	500	350
Revolutions per minute.....	130	160
Motor, kw.....	110	65
Revolutions per minute.....	485	580

The vacuum maintained at the pump inlet is usually from 25 to 30 cm. Hg. The maximum vacuum that can be attained is about 40 cm. Hg.

Cyclones and Filters

Cyclones.—The cyclones are of the usual cylindrical-conical type, and give a clearance of 88 to 90 per cent. Wear plates are provided on the inside surfaces at the points of inlet. Where very fine dust is handled it is advisable to install two cyclones in series. Two of the Giesche systems are equipped with double cyclones, and two with single units. Experience has shown that in general it is better practice to install two cyclones. Better clearance is maintained and the filters are less heavily loaded.

Filters.—The mechanical bag filters used on the vacuum systems are cylindrical in form with a motor-driven rapping mechanism and a discharge screw conveyor.

Each filter has 90 woolen bags 127 mm. in diameter by 2.5 m. long, and a total filter area of 90 sq. m. The required filter area depends upon

the fineness of the conveyed material, and the clearance through the cyclones. Experience at the Giesche plants has indicated that excess filter capacity is desirable. The filter at the Saeger roasting and sintering plant has the same bag area as those at the Waelz plant; i.e., 90 sq. m., although the displacement of the Saeger pump is only 39 per cent of that of the pumps at the Waelz plant.

Air Locks.—The material is discharged from the cyclones and filters by means of rotary air locks. If the material handled is exceptionally

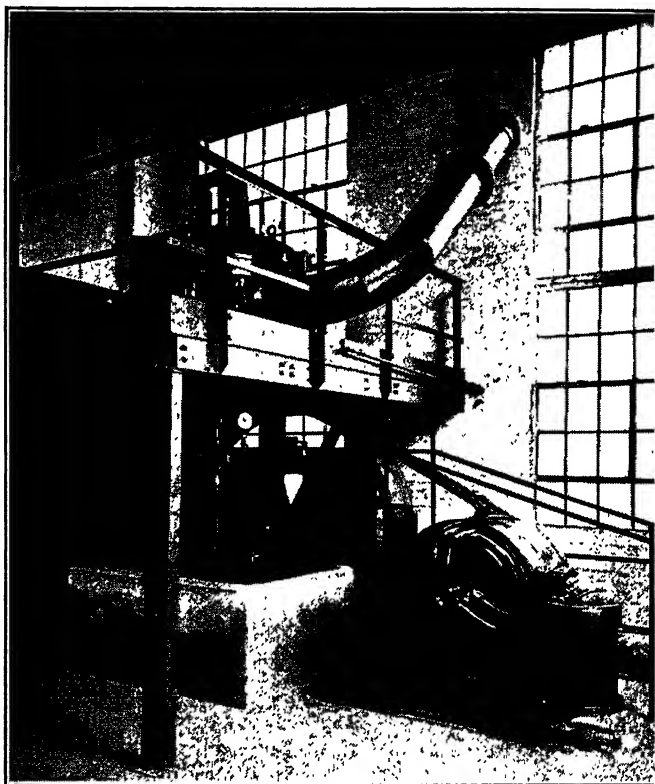


FIG. 6.—VACUUM PUMP, SAEGER PLANT.

abrasive, chilled cast iron or hardened steel should be used for the air-lock barrel liners, and for the edging strips of the rotors. The air locks must be as tight as possible, to prevent the entry of false air into the system.

“Raschig” Ring Spark Arrester.—The first installation at the Waelz plant was equipped with a special spark arrester between the second cyclone and the bag filter, to prevent glowing particles of flue dust from burning the filter bags. This arrester consists of a cylindrical tank filled with a series of removable boxes, each containing hundreds of small open tubes or “Raschig” rings, as they are called in Europe. The

boxes are covered top and bottom with wire mesh or expanded metal. The boxes, or containers are removed from time to time for cleaning in a rotating tumbler. This piece of equipment has proved very satisfactory. The filter bags are seldom burned.

Conveying Lines

Standard drawn pipe has been used for all permanent conveying lines. The portable pipes that are used in a number of places are made of 2.5 to 3-mm. plate, and are welded.

The inside diameters of the conveying pipes increase gradually between the pick-up points and the cyclones, in order to compensate for the gradual increase in vacuum and consequent increase in the volume

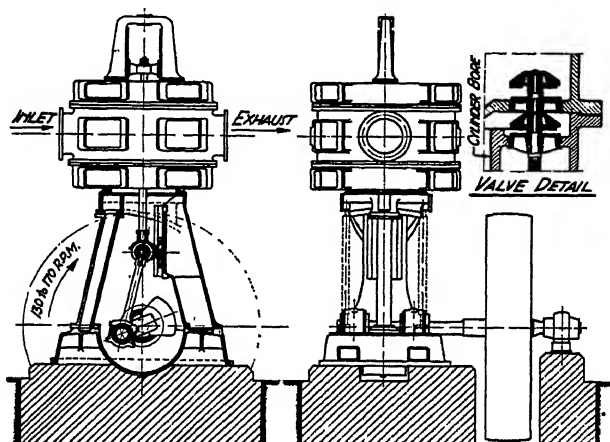


FIG. 7.—VERTICAL VACUUM PUMP.

of the air. Five pipe sizes are used at the Waelz plant, varying from 180 to 240 mm. inside diameters. The transport lines at the roasting and sintering plant vary from 125 to 150 mm. inside diameters.

It is important that the transport lines be kept absolutely airtight between the pick-up points and the cyclones. Air leakage must be prevented if maximum capacity is to be maintained. Where several branch lines with a number of pick-up points are required it is essential that the individual lines be equipped with cut-off valves, or blind flanges, to segregate the lines not in use. The air velocity through the conveying lines is from 45 to 50 m. per sec.; or from about 9,000 to 10,000 ft. per minute.

Vacuum Line.—The line connecting the cyclones and filters with the vacuum pump must be airtight, and of such size that the friction loss through it may be held to a minimum. The short vacuum lines at the Waelz plant have an inside diameter of 400 mm.; the two longer lines

510 mm. The vacuum line at the Saeger roasting and sintering plant has an inside diameter of 275 mm.

MATERIALS TRANSPORTED

Table 2 shows the physical and chemical make-up of the materials handled by the pneumatic equipment.

TABLE 2.—*Materials Handled by Pneumatic Equipment*

WAEŁZ PLANT*						
System	Material from	Zn, Per Cent	Pb, Per Cent	Cd, Per Cent	Specific Gravity	Tempera- ture, Deg. C.
I	Furnace dust chambers...	30-40	13-20		0.8-1.2	450-600
I	Vertical coolers.....	50-55	14-20		0.8-1.2	450
I	Horizontal coolers.....	50-58	14-17	0.4-0.6	0.7-1.0	100-300
II	Baghouses.....	50-58	14-17	0.4-0.6	0.6-0.8	50-60
II	Roaster flues.....	20-35	20-35	2.5-4.0	0.9-1.2	300-400
II	Vertical coolers.....	13-20	35-45	2.5-4.0	0.9-1.2	50-300
III	Roaster baghouses.....	10-13	45-56	3.0-6.0	0.9-1.2	50-60
III	Secondary plant.....	6-13	20-35	8-24	0.5-0.6	30-50

SÄEGER ROASTING AND SINTERING PLANT						
Material	Zn, Per Cent	Pb, Per Cent	Size	Specific Gravity	Mois- ture, Per Cent	Tempera- ture, Deg. C.
Baghouse dust.....	70	1.6	All minus 200 mesh	1.4-1.5	Dry	20-30
Flue dust.....	59	3.5	All minus 200 mesh	1.4-1.5	Dry	200-500
Cottrell dust.....	51	2.7	All minus 200 mesh	1.4-1.5	Dry	200-500
Zinc flotation concen- centrates.....			60 per cent minus 200 mesh	1.5-1.6	3.0-4.0	
Slack coal.....			0 to 5 mm.	0.7-0.8	5.0-8.0	

* All materials dry.

CAPACITY

The capacity of a pneumatic conveying plant depends upon the physical character of the material handled. Light and fluffy materials are more easily transported than heavy ones. Materials that are sticky, and that tend to pack together, such as lead fume and flotation concentrates, are not easily conveyed. The capacity when handling these materials is considerably reduced. The rate at which the material can be fed at the suction, or pick-up, points is obviously an important factor in determining the capacity of a pneumatic conveying unit. A regular and uniform feed should be maintained, as far as possible. The average

capacities of the Giesche pneumatic units for various materials are given in Table 3.

TABLE 3.—Average Capacities

WAE LZ PLANT ^a		
Material from	Metric Tons per Day	Metric Tons per Hour
1. Furnace dust chambers }	60	7.5
2. Vertical coolers }		7.0-7.5
3. Horizontal coolers	40	5.5-6.5
4. Raw oxide baghouses	75	15
5. Roaster dust chamber and flues }	8	3.0-4.0
6. Roaster vertical coolers }		3.0
7. Roaster baghouses	10	3.0
8. Secondary products plant	7	5.0-6.0
Total	200 metric tons	
Average pump-hours	25	
Average capacity	8 metric tons per hour per pump	
SAEGER ROASTING AND SINTERING PLANT		
1. Baghouse dust	3	8.5
2. Flue dust	4	3.0
3. Cottrell dust	8	2.25
4. Zinc flotation concentrates ^b		
5. Slack coal	12	3.0
Total	27 metric tons	
Operating time	8.5 hr.	
Average capacity	3.18 metric tons per hour	

^a Both pumps operate at the same time, but on separate systems.

^b Only small amounts of this material are conveyed to the sintering machine feed hoppers.

The guaranteed capacities of the equipment when conveying average materials was given by the manufacturers at 10 and 5 metric tons per hour for installations at the Waelz plant and the Saeger roasting and sintering plant, respectively. In practice it has been found that the pneumatic units have larger capacities than guaranteed when fine dry materials are transported.

CONSTRUCTION COSTS

It is difficult to give comparative costs because the Giesche plants have been built over a period of eight years, and during that time there

have been a number of price changes and currency devaluations. However, in order to give some idea of the construction costs in Poland, the actual costs, in Polish zloties, have been converted to the present devaluated dollar (59.06 cents), and are shown herewith in dollars per ton of rated conveying capacity:

PNEUMATIC EQUIPMENT AT	CONSTRUCTION COST PER TON CAPACITY
Waelz plant.....	\$16,000.00
Roasting and sintering plant.....	5,300.00

Had the plants been completed before the devaluation of the dollar, the construction costs would have been about 40 per cent less for the part of the equipment installed since 1933.

The wide variation in construction costs per ton of installed capacity at the two plants is due to the difference in the size and number of individual units. The Waelz plant is equipped with three pneumatic units, whereas the sintering and roasting plant has but one unit. The unit cost can thus be considered as approximately the same at both plants; i.e., \$5300 per ton of installed conveying capacity.

DESIGN

The design for the pneumatic systems at the Giesche plants were worked out by the engineers and metallurgists of the Giesche Spółka Akcyjna in collaboration with the equipment manufacturers.

So far as we know, the pneumatic system installed at the Waelz plant in 1930 was the first in which flue dust at a temperature of 600° C. was successfully transported.

While pneumatic conveying has proved economical and practical at the Giesche plants, it should not be considered a "cure-all" for all troublesome conveying problems. Before installation of pneumatic conveying equipment for any particular material, tests should be carried out in order to determine the behavior of the material through the system.

No set rules can be established for the design of pneumatic conveying systems. Every plant and every material requires special treatment. The experience at the Giesche plants, however, has shown that it is advisable to install oversize pumps, filters with excess capacity, and large-diameter conveying lines. Lines under 5-in. inside diameter should be avoided.

Production of Electrothermic Zinc at Josephstown Smelter

BY GEORGE F. WEATON,* H. K. NAJARIAN,† AND CARLETON C. LONG,‡
MEMBERS A.I.M.E.

PARTIAL descriptions of the operation of the St. Joseph Lead Company's Josephstown smelter have been published. In 1936 the electrothermic production of zinc oxide was described;¹ in 1939 appeared a description² of the electrothermic method of producing zinc metal. Inasmuch as the plant capacity has more than doubled, and in view of the fact that operating practices have improved greatly since these publications, it seems worth while to prepare a fresh description of the present-day electrothermic zinc plant and practice.

Josephstown smelter is situated on the south side of the Ohio River about 3 miles below its confluence with the Beaver River. In addition to river barge, the smelter is served by Pennsylvania state highway No. 18 and by a spur line of the Pittsburgh and Lake Erie Railroad (N.Y.C.). A recent extension of this spur line connects with the Pennsylvania Railroad.

As originally contemplated the plant was to handle only the product of the company's own mines in St. Lawrence County, New York, but owing to the incessant demand for zinc and zinc oxide, it has been necessary to supplement New York concentrates with foreign ores (principally from Quebec and the Argentine).

The general operational procedure followed comprises roasting the sulphide concentrates, converting the sulphur dioxide

into sulphuric acid, preparation of a strong-structure sinter from the calcine, crushing and sizing of coke, reduction of coke-sinter mixture by electrothermic means, condensation of the evolved zinc vapor to make zinc metal or burning of the zinc vapor to make zinc oxide, collection and packing of the zinc oxide. Dusts recovered by the roaster and sinter Cottrells are treated in the leach plant for separation of lead sulphate, cadmium metal and zinc sulphate. The general flowsheet is shown in Fig. 1.

PRINCIPAL ITEMS OF EQUIPMENT

Roaster Plant

Concentrate drier, 6-ft. dia. by 40 ft. 5 in., countercurrent, direct gas-fired.

3500-ton concentrate storage in three vertical steel tanks.

Five modified Nichols-Herreshoff twelve-hearth roasters, 21 ft. 6 in. in diameter.

Four fans for shaft-cooling air.

One three-drum Stirling water-tube waste-heat boiler, 428 hp., 200 lb. per sq. in., with connections to upper and lower balloon flues.

Direct gas-fired countercurrent rotary-kiln roaster for Cottrell dust.

Necessary conveying equipment, described below.

Instrumentation consists of: draft indicators, (3d hearth); various manometers; pyrometer served by thermocouples in each hearth, entrance and exit of waste-heat boiler, entrance and exit of each hot Cottrell; roaster draft recorder and shaft air-pressure controller; temperature recorder and controller (10th and 12th hearths); SO₂ recorder (waste-heat boiler

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¹ References are at the end of the paper.

exit); compressed SO₂ gas pressure recorder (soot blowers); remote-reading ammeters on each roaster-shaft drive motor; vacuum recorder (exit waste-heat boiler).

6 lb. per sq. in., and one standby Roots-Connersville positive displacement blower.

Three contact units each consisting of: three shell and tube heat exchangers; two

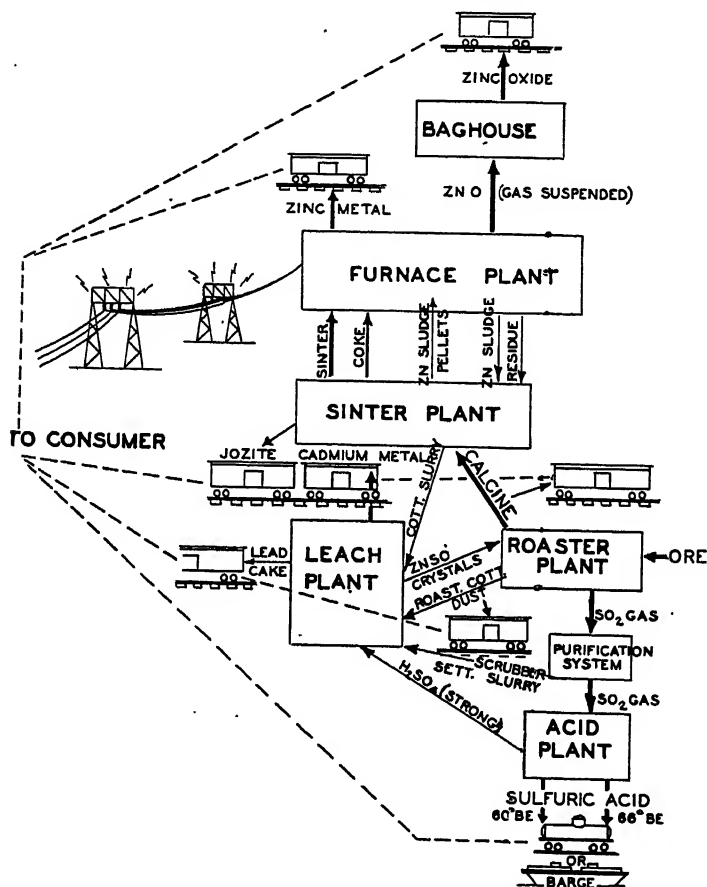


FIG. 1.—GENERAL FLOWSHEET OF ELECTROTHERMIC ZINC PLANT AT JOSEPH TOWN SMELTER.

Acid Plant

Two SO₂ gas purification systems, each consisting of: plate and frame Cottrell precipitator, tile-packed cooling tower, sludge settler and circulant coolers.

Acid-mist Cottrell precipitator.

Coke filter.

Dry towers and dry-tower acid coolers.

Gas-pumping installation consisting of three pumps of 15,000 cu. ft. per min., 6 lb. per sq. in.; one 12,000 cu. ft. per min., 6 lb. per sq. in.; one 6000 cu. ft. per min.,

V₂O₅ catalyst converters; one SO₃ cooler, recirculated-air type; one SO₃ absorber; together with associated acid coolers, pumps, batch and product tanks, car-loading platform, barge dock, etc.

One cold-unit preheater serves all three contact systems.

Instrumentation, besides usual thermometers, hydrometers, and manometers, consists of: two contact-making temperature indicators in each cooling tower; vacuum recorders at entrance to each final

filter (coke box); vacuum recorders on blower intake headers; SO_2 content recorders on each blower exit header; H_2SO_4 content recorders on each absorber acid-pump-tank circuit; smoke detector on absorber exit gas; recording tail-gas flow-meter; remote-indicating acid-level gauges on important tanks.

Leach Plant

Lead and brick-lined solution tanks.

60-ft. diameter lead and brick-lined Dorr thickener.

Propeller-agitated cadmium-precipitation tanks.

Various filter presses and pumps (principally Wilfley Hastelloy C).

Two cast-lead horizontal-tube evaporators, 5 ft. 0 in. and 6 ft. 0 in. diameter.

Two vacuum crystallizers, 8 ft. 6 in. and 9 ft. 6 in. diameter.

One lead rotary vacuum crystal filter, 4 ft. 0 in. diameter by 2 ft. 0 in. face.

One modified Rotolouvre crystal drier, 11 ft. 6 in. diameter by 35 ft. 0 in. long, with associated fans, stoker-fired furnace, dust-recovery means and conveying equipment.

One Harding conical ball mill, 6-ft. diameter by 22 inches.

Instrumentation consisting of: temperature recorders (vacuum crystallizers), temperature controllers (on warm and on hot air supplied to drier), air-flow pressure controllers (on drier), draft gauges, etc., on drier.

Sinter Plant

Storage bins for raw-mix ingredients plus feeders to mix-collecting belt discharging into rotary drum mixer and pelletizer.

Raw-mix surge bin equipped with rotary discharge table and five adjustable diver-sion blades.

Three 42-in. by 44-ft. and two 42-in. by 22-ft. Dwight-Lloyd sintering machines with gas-fired igniters.

Three fans, 30,000 cu. ft. per min. at 14 in. H_2O .

Two fans, 20,000 cu. ft. per min. at 15 in. H_2O .

One Cottrell exhaust fan, 130,000 cu. ft. per minute.

One rod-curtain Cottrell precipitator with preceding water-sprayed gas-conditioning tower.

One 300 by 11-ft. (top diameter) Custodis radial brick stack.

Two roll crushers with associated sizing and conveying equipment and storage bins.

Instrumentation consists of: pressure gauges and manometers; temperature recorders at entrance to conditioning tower and at each Cottrell exit; recording flow-meter (gases from sintering-machine fans); vacuum recorder (entrance of conditioning tower).

Coke Plant

Railroad receiving hopper, roll crusher, rod mill, trommels, conveying equipment, bins, described further in succeeding pages.

Residue-treatment Plant

Trommels; three magnetic separators; air-blast coke-sinter separator; bins; coal-fired rotary kiln for drying blue powder recovered from condenser-gas dedusters.

Furnace Plant

Nine storage bins for sized sinter.

Nine storage bins for sized coke.

Nine storage bins for dried blue powder.

Twenty-seven constant-weight feeders.

Nine direct gas-fired countercurrent rotary kiln charge preheaters, 4-ft. dia. by 17 ft. 3 inches.

Five 69-in. i.d. shaft electric furnaces for producing metal.

One 96-in. i.d. shaft electric furnace for producing metal.

Two 69-in. i.d. shaft electric furnaces for producing oxide.

One 96-in. i.d. shaft electric furnace for producing oxide.

Shaft height varies from 38 to 40 feet.

Rotary feed distributors and rotary discharge tables.

Five 22-ft. and one 31-ft. condensers with associated gas-washing equipment.

Power-distribution facilities comprising fifteen 1500-kva., 66/2.3 kv., 60-cycle, single-phase transformers; forty 500-kva., 2300/320/160-volt single-phase furnace transformers with auxiliary oil coolers; forty plus-or-minus 10 per cent, 2300-volt, 50-kva. induction voltage regulators.

Electrodes, electrode clamps, etc.; four single-phase circuits in each 69-in. furnace; six single-phase circuits in each 96-in. furnace. Upper and lower electrode groups are 26 ft. apart.

Oxidation manifolds and oxide-carrier ducts (oxide furnaces only).

Multipanel continuous-cleaning air filters for oxidation and cooling air.

Instrumentation consists of: pyrometers served by thermocouples in oxidation manifolds and in condensers; vacuum indicators and vacuum recorders on each metal furnace at region of vapor offtake; temperature and draft controllers for each preheater; electrical control panel comprising volt, ampere, kilowatt and kilowatt-hour meters on primary (2300-volt) side of furnace transformers. Each electrode circuit is served by voltmeter and ammeter and by a power-controlling wattmeter.

Oxide-collecting System

Each 69-in. oxide furnace is served by one fan of 30,000 cu. ft. per min. nominal capacity.

The 96-in. oxide furnace is served by two fans of the same capacity. Each fan is served by a cyclone-type classifier.

Filter bags are of cotton, 60-in. circumference by 45 ft. long, and are grouped in 14 units of 50 each.

Automatic shakers are provided for each 50-bag unit.

Collected oxide is handled, entirely

mechanically, by screw conveyors and bucket elevators.

Calcination equipment is available for manufacture of specialty pigments.

Warehouse, control laboratory, shipping and loading facilities are available.

Instrumentation consists of: temperature and pressure recorders on each group of bag units; pyrometer served by thermocouples in each fan case and in calcination apparatus.

General Service Facilities

Well-equipped machine, electrical, carpenter, blacksmith and steel fabricating shops.

Modern change houses for men and women, individual lockers, etc.

Well-equipped analytical, physical testing, microscopic, paint and rubber laboratories for both control work and research activities.

Cafeteria, beef and pork requirements supplied by the company's farming operations adjacent to the smelter.

Description of Operations

The accompanying flowsheets depict the essential features of the various operations conducted at Joseph town smelter. Some general observations, experience, operating data and description are given below.

Roaster and Acid Plants

Zinc sulphide flotation concentrates, shipped in box cars, are unloaded manually with a conventional automatic-clutch, power-drawn scoop with stainless-steel face. Frozen concentrates are given a period of residence in the thawhouse. Concentrates from the New York mines contain about 3 per cent water and are conveyed by bucket elevator to storage tanks. Wetter ores are passed through the concentrate drier before storage.

Withdrawal of concentrates from storage is accomplished by apron feeders discharg-

ing onto a gathering belt. By adjusting the discharge rate of the individual feeders, various species of ore can be mixed in

are 8 per cent Fe and 0.4 per cent Pb maximum. For the two-year period 1942 and 1943, there were roasted 228,102 tons of

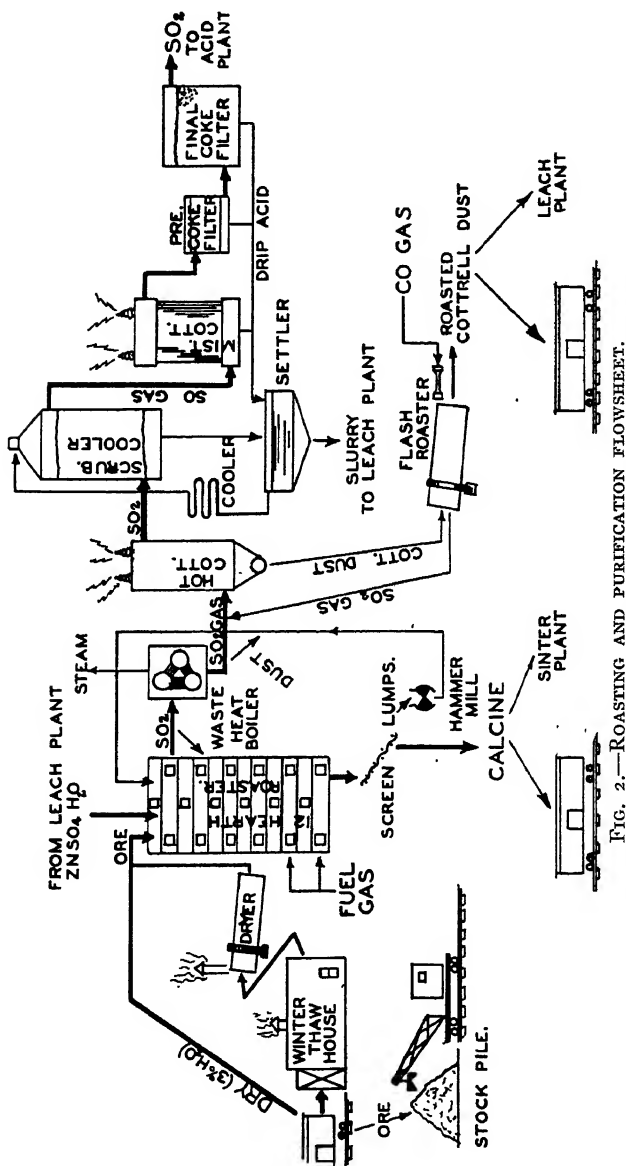


FIG. 2.—ROASTING AND PURIFICATION FLOWSHEET.

proportions considered desirable. In general, feeders are adjusted to control the iron and lead content of the mixture within certain limits. Currently the specifications

concentrates made up from 149,504 tons of Balmat and Edwards (N. Y.), 63,032 tons of Quebec, 14,295 tons of Aguilar (Argentina), and 1271 tons of Toplin.

Typical chemical and screen analyses of these concentrates are given in Table 1.

Concentrates pass over a weightometer on their way to the individual surge bins,

crystals in the upper hearths of the roasters counteracts, in part, temperature rise from sulphide oxidation and hence permits more economical use of air. Natural gas, to the

TABLE 1.—*Typical Analyses of Concentrates Roasted in 1942 and 1943*

Source	CHEMICAL ANALYSES, PER CENT											
	Zn	Pb	Cu	Cd	Fe	Insoluble	SiO ₂	CaO	MgO	Al ₂ O ₃	S	Mn
Balmat.....	54.93	0.55	0.10	0.14	7.5	2.4	1.9	0.6	0.6		32.1	0.25
Edwards.....	58.90	0.27	0.04	0.10	6.0	0.7	0.6	0.5	0.5		32.7	0.14
Quebec.....	52.75	0.07	0.75	0.13	11.2	2.0	1.5	0.15	0.1		32.9	0.19
Aguilar.....	53.5	2.9	0.29	0.17	5.5	2.8	2.5	0.4	0.1		31.5	1.5

TYPICAL SCREEN ANALYSES, TYLER STANDARD SIEVES, PER CENT							
Source	+48	-48 +65	-65 +100	-100 +150	-150 +200	-200 +325	-325
Balmat.....	4.5	16.7	13.8	11.9	9.1	13.8	30.2
Edwards.....	0.1	1.9	8.7	14.0	14.0	15.9	45.4
Quebec.....	0.2	0.5	3.5	7.8	12.0	14.4	61.6
Aguilar.....	0.5	1.7	6.4	13.5	11.1	16.7	50.1

of approximately 8 tons capacity over each roaster. Conveyance is by belt bucket elevator and rubber belt. Concentrate is fed from the surge bins onto the drying hearth of the roaster. On the two older roasters feeding is accomplished by knife blades attached to the central rotating shaft. The three newer roasters are equipped with adjustable-gate apron feeders. The knife feeders are the less desirable of the two; neither is wholly satisfactory, as they do not cope with change in physical characteristics of the ore leading to nonuniformity in mass of ore introduced into the roaster per unit time.

Concentrate, partly dried by rabbling across the top hearth, enters the roaster proper through drop gates sealed by bell and crank arm. Ignition commences on the first hearth. Hearth temperatures are controlled by variation in location of points of air introduction. In general, the lower down in the roaster the air is introduced, the higher will be the upper hearth temperature. Zinc sulphate crystals, from the leach plant, are mixed with the concentrate feed. Endothermic decomposition of these

extent of 900 to 1000 cu. ft. per ton of concentrates, is burned in the 10th and 12th hearths by tangentially directed inspirating burners. The purpose of burning gas is to heat incoming air up to roasting temperature.

Temperature distribution among the hearths is illustrated by the set of pyrometer readings for a roaster handling 70 tons of concentrates per day (No. 4 roaster, 4/10/44) given in Table 2.

TABLE 2.—*Temperature Distribution*

Hearth Number	Temperature, Deg. C.	Hearth Number	Temperature, Deg. C.
1	750	7	900
2	970	8	840
3	980	9	840
4	960	10	820
5	950	11	780
6	920	12	710

With the ores at present being handled, hearth temperatures much above 1000°C. are usually accompanied by "snowballing" of the burden, which, if allowed to pile up, may bend the rabble arms.

Rabble arms, cast of 28 per cent chromium alloy, are air-cooled by coaxial tube supplied with air from the air duct of the

so introduced is regulated by opening or plugging orifices and by varying the annulus air pressure.

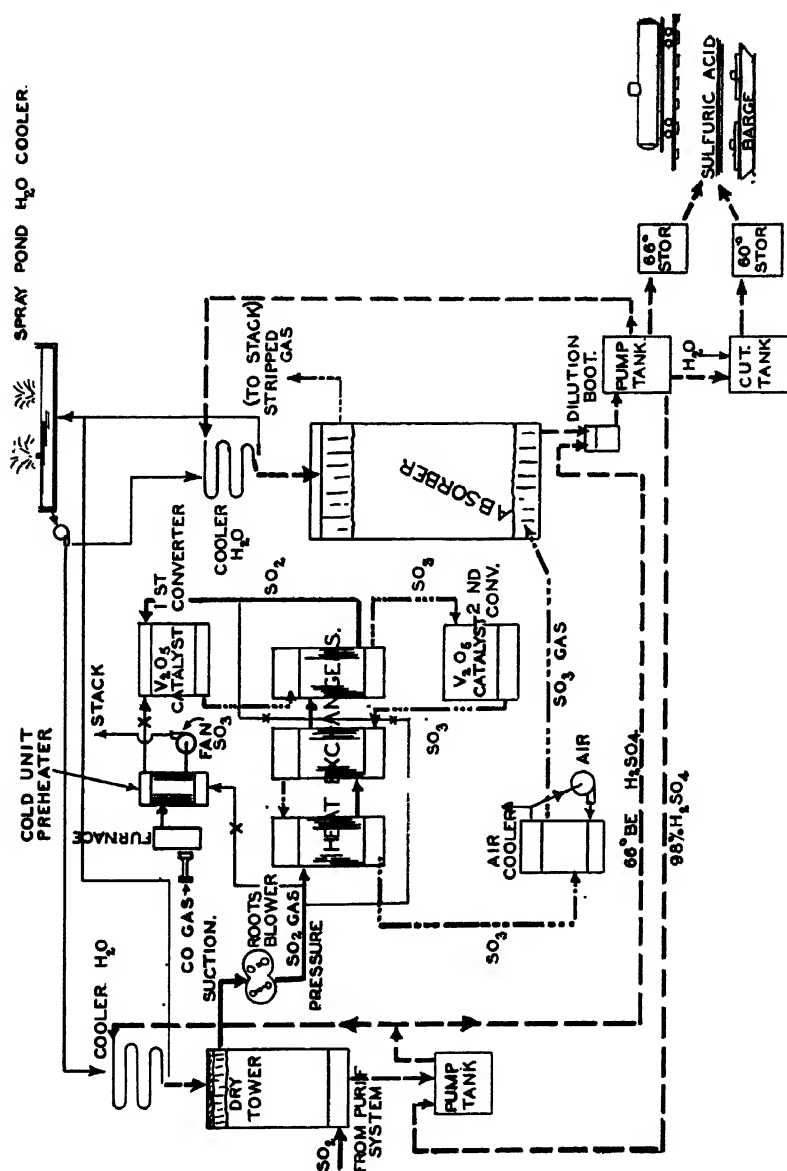


FIG. 3.—FLOWSHEET OF ACID PLANT.

inner shaft. A portion is passed to the lower hearths, for oxidation air, through a number of $1\frac{1}{2}$ -in. dia. orifices in the outer wall of the shaft. Amount of preheated air

Rabbles are cast from 28 per cent chromium alloy. Refractory (SiC) rabbles have been employed with satisfactory results but are not interchangeable on the same

arm with metal rabblies. Rabble consumption is about 0.14 lb. per ton of concentrates. Rabble-arm shaft-rotation rate is about one revolution per minute.

Calcined ore discharges from the roaster across a grizzly and into a 16-in. water-cooled screw conveyor. This in turn discharges into a chain-bucket elevator feeding a trommel equipped with a 0.140-in. opening Ton-Cap screen. Oversize is hammer-milled and returned to concentrate feed. Undersize proceeds by means of Jacoby conveyor to 900-ton calcine-storage bin. Average analysis of calcine for 1942 and 1943 is: Zn, 65.06 per cent; Pb, 0.045; Cu, 0.3; Cd, 0.10; Fe, 8.8; insoluble, 2.2; SiO₂, 1.8; CaO, 0.6; MgO, 0.5; S, 2.6; Mn, 0.3.

Of the lead in the concentrates, about 10 per cent appears in the calcine, the remainder going into the Cottrell dust and purification-system residues. About 25 to 30 per cent of the cadmium is eliminated by the roasting operation.

Roaster gases, containing 7.0 to 7.5 per cent SO₂, pass through a brick-lined balloon flue to the waste-heat boiler and from the boiler are distributed by an unlined steel-plate balloon flue to each of the two gas-purification systems. Gas temperature is 720°C. entering the boiler, 420°C. leaving the boiler, 320°C. entering the dust Cottrell and 290°C. entering the cooling tower.

The cooling towers are packed with 6-in. and 3-in. single spiral rings to a height of 13 ft. Tile area is approximately 50 sq. ft. per pound of gas per minute. Irrigation rate is about 15 lb. per min. for each square foot of cross section. Circulant is zinc sulphate solution containing 30 to 50 grams of H₂SO₄ per liter. A bleed-off to the leach plant controls circulant concentration.

Settled sludge joins the lead-containing residue product of the leach plant. Drip acid from the mist Cottrells and coke filters is returned to the cooling-tower circuit. The

amount of acid in the drips is 1 per cent of total acid production.

Clarified circulant is pumped through lead-tube coolers composed of bundles of 1½-in. i.d. tubes manifolded to provide a flow rate of 2 to 3 ft. per sec. The decks of tube bundles are irrigated with well water, which seldom exceeds 16°C.

Cooling-tower exit gas temperature is controlled so that the amount of water vapor in the gas entering the drying towers per unit time will, when mixed with the acid made by the absorbers in the same period of time, yield a solution containing 93 to 95 per cent H₂SO₄ (commercial 66° Bé acid contains 93.19 per cent H₂SO₄). As far as known, the cooling-tower unit installed in 1937 represents the first commercial practice of close-circuiting the cooling tower with a clarifier and elimination of acid losses to sewer.

Gas from the cooling tower passes next through two exposed-tube mist Cottrells in series, thence through a preliminary filter, 6 in. of 2 to 5-mesh coke, followed by a final filter of a 4-ft. bed of coke grains of graduated sizes ranging from 1½ in. down to 20 to 40-mesh (12 in.). The final filter exits connect with a header, which distributes gas to the four drying towers.

Drying is accomplished by contact with 93 to 95 per cent H₂SO₄. Transfer surface, provided in the main by 3-in. triple spiral rings, is about 100 sq. ft. per pound of gas per minute. Drying-tower acid is recirculated through pump tanks and trombone-style coolers consisting of 6-in. cast-iron pipe externally irrigated with water. Acid "make" is bled off continuously to a surge tank. This tank supplies acid for product batches and also dilution acid for the SO₂ absorption system. Absorber acid "make" flows to the drying-tower pump tanks.

Gas from the drying towers should, ideally, contain not over 5 mg. of water vapor per cubic foot of gas and not over 0.02 mg. of sulphuric acid (mist) per cubic foot. At present driving rates these limits

are often exceeded, with consequent effect in the contact system. The purification system is being operated at 140 per cent of rated capacity and the contact system at 180 per cent of nominal capacity. In order to accomplish this, it was necessary to replace the original low-pressure blowers with high-pressure blowers. The differential pressure across the blower system is 6 lb. per sq. inch.

Blower gas is distributed to the three contact units. Here gas passes through the shell side of the three heat exchangers, through the first catalyst chamber, through the tube side of the third heat exchanger, through the second catalyst chamber, back through the tube side of the first two heat exchangers, through the tube side of the SO_3 cooler, thence to the absorber and, stripped of SO_3 , through the tail-gas trail to the 300-ft. stack. Temperature of gas entering the catalyst chambers is normally in the 400° to 425°C. range and is controlled by suitable heat-exchanger by-pass valves.

Catalyst (of Monsanto manufacture) is vanadium pentoxide supported on a suitable base, taking the form of rods about $\frac{3}{16}$ -in. dia. by $\frac{3}{16}$ in. long. Catalyst mass is laid on crushed firebrick carried on a screen. With the high driving rate it has been found desirable to lay a screen on top of the catalyst bed to prevent blowholes and consequent gas channeling. At normal driving rates conversion of SO_2 (5.5 to 6.5 per cent in blower gas) to SO_3 averages 95 to 97 per cent, but with the present overload the conversion rate has fallen to 94 to 95 per cent and on occasion even lower.

Absorbers are packed with 3 by 3-in. triple spiral rings. Transfer area is about 55 sq. ft. per pound gas per minute. Acid entering the absorber contains 98.5 to 99.0 per cent H_2SO_4 , the exact concentration being continuously measured and recorded by Leeds and Northrup conductivity apparatus. Acid temperature is con-

trolled with reference to the temperature of the entering SO_3 gas, being about 100°C. with 260°C. gas and 70°C. with 170°C. gas.

The adjustment of the relation between absorber acid temperature and gas entrance temperature is no mere whim. It is one part of a comprehensive operational procedure developed several years ago to produce mist and fume-free absorber exit gases. A limebox neutralizer is no longer necessary; tail gases, under the scrutiny of a photovoltaic cell, pass directly to the stack.

Commercial product acid is prepared batchwise by dilution of excess drying-tower acid. Of the total acid produced (100 per cent equivalent H_2SO_4 basis), approximately 75 per cent is made into 66°Bé (93.19 per cent H_2SO_4) product; the balance is further diluted to 60°Bé (77.67 per cent H_2SO_4). Shipment is by rail or barge.

Sulphur dioxide gas is handled in steel-plate-enclosed equipment while hot and in chemical-lead enclosures from the cooling towers to the drying towers. Dry-gas ducts are of steel, as are the heat exchangers, etc. For weak acid, chemical-lead pipe and valves are employed with complete satisfaction while for acid of 60°Bé and stronger, cast iron is used, but with rather frequent trouble from imperfections in the metal. Strong-acid valves are of Durimet. Most of the important pumps are now of the no-stuffing-box type. Illium (or equivalent alloy) impellers and fittings are standard.

Leach Plant

The primary purpose of the leach operation is to provide an outlet for the bleed-off solution of the acid-plant cooling-tower circulant. If this were not provided, the zinc sulphate content of the cooler circulant would increase to the crystallization point; also, there would be no outlet for the acid drips from the mist Cottrell and coke filter. Advantage is taken of the fact that there are available two by-product materials—roaster-plant and sinter-plant Cot-

separately slurried and pumped to the leach-plant batch tanks, where it assists in reducing the ferric iron content of the solution. Final traces of trivalent iron are removed by addition of a few kilos of blue-powder mud.

Completed batches, neutral (green) to xylene cyanole modified methyl orange,³ flow to the Dorr thickener. Cadmium is removed from the clarified liquor (1 to 2 grams Cd per liter) by agitation with zinc dust at 55° to 60°C. followed by filter pressing. Filtrate, containing about 150 grams Zn per liter, enters the evaporator-crystallizer-crystal filter circuit. Mother liquor from the crystal filter returns to the evaporator. This circuit is kept acid (10 to 20 grams H₂SO₄ per liter) to avoid aerial oxidation of ferrous iron, the gelatinous products of which would diminish the permeability of the crystal filter screen.

Sulphate crystals are dried by a Rotolouvre drier modified according to the suggestion of W. B. MacBride, Chief Engineer. The modification consists in supplying relatively low-temperature air (100°C.) to the wet crystals, followed by application of warmer air (260° to 270°C.) after removal of the first molecule of water of crystallization. The importance of this technique becomes apparent when it is noted that there exists a spread of but 11°C. between the decomposition temperature of ZnSO₄·7H₂O and the effective melting point.

Crystals ordinarily are dried only sufficiently (approx. 30 per cent water content) to permit mechanized handling unless some unusual condition, such as very wet ore, makes further drying of crystal feed advantageous. The dried crystals are added to the concentrate elevator when ore is being conveyed to the roaster feed bins.

Underflow from the Dorr thickener formerly was leached with stronger acid (170 to 200 grams per liter). Since the introduction of zinc-recovery means from lead blast-furnace slag at Herculanum

smelter, the underflow is filtered and shipped without leaching. A further advantage of this procedure is that much of the iron (desirable in the lead blast furnace) remains with the lead sulphate residue if it is not leached.

Crude cadmium sponge is dried, oxidized, redissolved in sulphuric acid, purified by controlled additions of zinc dust, filtered, and pumped to a cementation tank. Here a relatively pure cadmium sponge results from metathesis with slabs of Bunker Hill zinc. Gathered sponge is pressed into firm cakes (of approx. density 5.6 grams per c.c.), which are then distilled in graphite bottles. The distillate is melted under caustic (NaOH) and cast into commercial shapes, usually sticks. Cadmium content is 99.97 to 99.98 per cent. Pumps originally were of the stuffing-box type but for the most part have been replaced by the no-stuffing-box (Wilfley) type with all wetted parts made of Hastelloy C.

Sinter Plant

The principal purpose of sintering is to agglomerate the calcine into properly sized particles sufficiently robust to avoid crushing while descending through the electric furnace. Derivative benefits of sintering are further elimination of sulphur, lead and cadmium.

Sinter components are calcine, returned sinter fines, silica sand, crushed coke, fines screened from furnace residues, sinter-plant dust-collector dust, furnace-plant dust-recovery dust.

A typical mix-room sheet shows: calcine, 400 lb. per min.; return sinter fines, 1050; silica sand, 19; coke, 68; residue fines, 30; dust-collector product, SP, 38; dust-collector product, FP, 25. The silica sand is added for a flux, which makes the sinter hard and strong even though porous and lacelike.

Sinter composition is shown by the following average analysis for 1942 and 1943: Zn, 59.89 per cent; Pb, 0.037; Cd, 0.007;

Fe, 9.0; insoluble, 8.2; SiO_2 , 8.0; CaO, 0.8; MgO , 0.6; Al_2O_3 , 2.0; S, 0.5; loss on ignition, about 0.5 per cent.

charges into the raw-charge mixer, which consists of a horizontal rotating cylinder containing a pug-bladed shaft rotating in

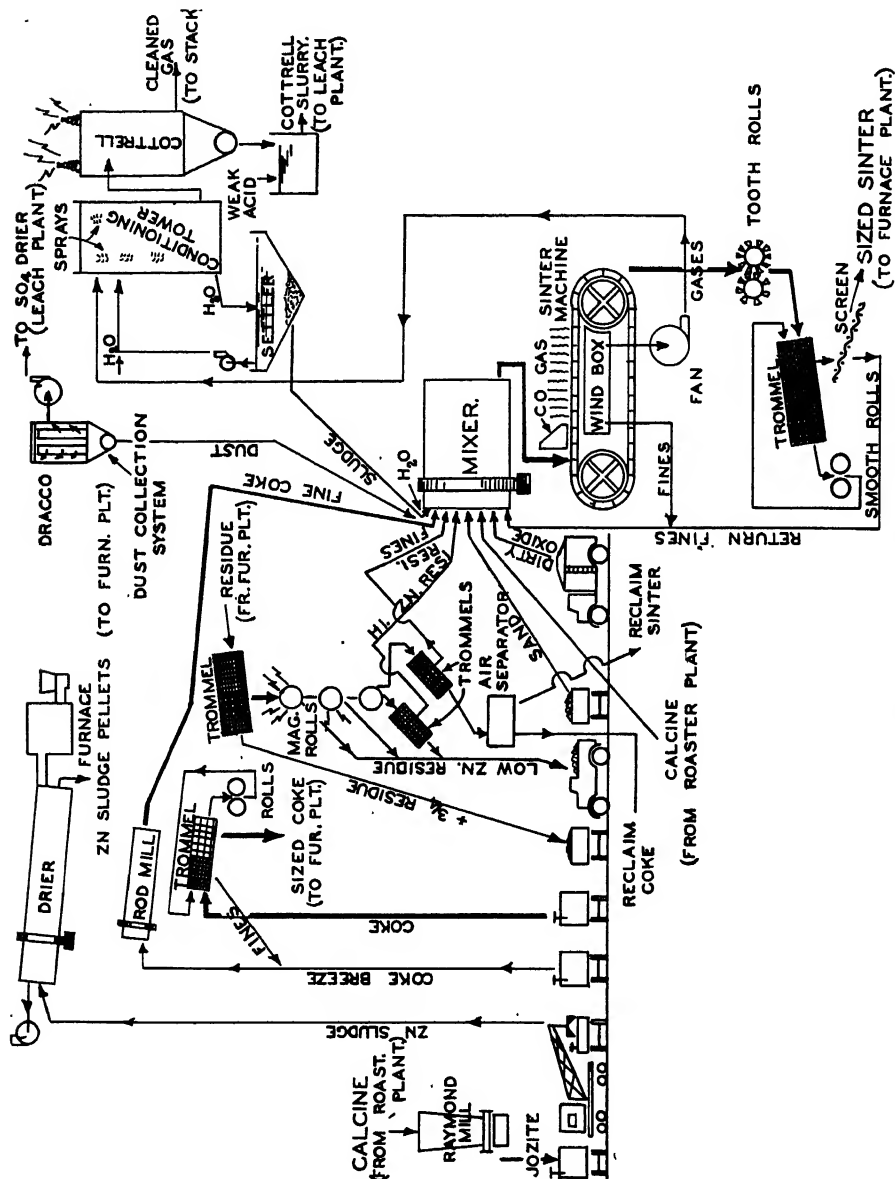


FIG. 5.—RESIDUE TREATMENT AND SINTERING.

Sinter-mix components are fed from their respective bins by constant-volume feeders of either the belt or apron type, with adjustable orifices. A collecting belt dis-

position to the movement of the charge imparted by the cylinder. Water is introduced to the extent of about 11 per cent of the dry weight of the charge, though the

actual amount of water to be added is judged by the appearance and coherence of the mix, the desired condition being one of nodulization.

Belt elevator and belt conveyors transfer the raw mix to a rotary-table feed distributor, where chain-wheel operated and adjustable diversion blades claim feed for belt conveyors leading to the individual sintering machines. Charge is distributed on the pallets by an oscillating chute formed of discarded rubber belting, to which the wet-mix fines do not readily adhere.

Bed thickness varies from 10 to 13 in.; the thicker beds being preferred when the calcine composition is uniform and the windbox air seals are adequately maintained. Ignition is accomplished by burning condenser gas (carbon monoxide) in a muffle of local design, characterized by a heat release per unit volume ratio relatively lower than that of conventional igniters. Pallet grates consist of simple cast-iron bars, half as long as the pallet, laid lengthwise of the pallet and supported by a transverse center bar. The introduction of this grate bar⁴ and a grate-bar knocker (cleaner)⁵ reduced grate-bar consumption costs to less than 10 per cent of that for conventional grates. New grate bars are added without slowing down the machine. Pallets are of cast steel.

Burned sinter drops from pallets into a pan conveyor leading to a set of slugger (tooth) rolls. Preliminary crushed product passes, by pan conveyors, over a $\frac{3}{4}$ -in. trommel, of which the oversize is in closed circuit with a pair of smooth rolls. Undersize proceeds by chain-bucket elevator, to a double trommel yielding three products: $-\frac{1}{4}$ in., $+\frac{1}{4}-\frac{1}{2}$ in., and $+\frac{1}{2}$ in. The two latter are binned separately and mixed in proportions required to yield specified size distribution for furnace feed. The $-\frac{1}{4}$ -in. product is returned to the raw mix. From 2.5 to 2.6 tons of sinter is

thus recirculated for each ton of sized sinter produced.

One ton of dry concentrate yields about 0.83 ton calcine, of which, in turn, one ton yields 1.17 ton sized sinter, or about 0.97 ton sinter per ton dry concentrate. Production rate (1942 and 1943) was 0.70 lb. size sinter per sq. ft. of grate area each minute operated. Pallet loading was 2.7 lb. raw mix per sq. ft. each minute.

Combustion fuel is supplied by crushed coke, by carbon in the residue fines and by residual sulphide sulphur. The apparent carbon equivalent is 3.4 per cent of the raw mix. Sintering temperature, as estimated by traveling thermocouple, is of the order of 1600°C.

Elimination of cadmium is an important function of the sintering operation. Of the cadmium in the calcine entering the sinter-furnace-residue circuit, approximately 1.8 per cent appears in the metal productible. Similarly, about 27.5 per cent of the calcine lead appears in the zinc products. Over-all elimination in the year 1943, from concentrate to metal productible was 97.2 per cent for the lead and 98.8 per cent for the cadmium.

Coke Preparation

Two coke materials are purchased from by-product producers, breeze coke and pea coke. From the latter is prepared sized coke for the electric furnace. The fines from this sizing operation, together with the breeze coke, are crushed in a rod mill to produce fuel for the sintering operation.

Furnace coke is sized by passage through a trommel (0.693 to 0.756-in. opening), oversize returned to trommel after passage through double-roll crusher, followed by a second trommel (0.140-in. screen opening) from which the oversize represents sized coke while the undersize joins the breeze coke. This material is crushed by a 5-ft. 0-in. dia. by 10-ft. 0-in. long peripheral slot-discharge rod mill to approximately 20 per cent $+10$ -mesh, 35 per cent $-10+20$ -

mesh, and 45 per cent—20-mesh, and containing about 15 per cent moisture. Consumption of rods (2.5 in. max. dia., 0.75 to 1.0 per cent C, 1.0 per cent Mn) is slightly less than one pound per ton of coke crushed. Coke rolls are hard-surfaced with high-carbon rod about every 7000 to 8000 tons of coke crushed. Coke conveying is by rubber belts and bucket elevators. Chute liners are white iron or stagnant coke layer or, more recently, salvaged firebrick.

Total coke consumption is 0.85 ton per ton of zinc equivalent produced, of which 0.27 ton represents coke fines for sintering while 0.58 ton is sized coke for the electric furnaces. These ratios are somewhat higher than those experienced (0.75) with feed of higher grade zinc concentrate.

Residue Separation

As described more fully below (see also Fig. 5), furnace residue falls from the rotary discharge tables onto a pan conveyor and by a series of such conveyors reaches a trommel in the residue plant. Separation is made here of material that is to be immediately discarded from material to be further separated. This separation is based on the theory, born out by experience, that residue particles larger than the largest particles entering the furnace have lost the major portion of their zinc, with the result that the melting point is lowered sufficiently to permit slagging and agglomeration. A 0.756-in. opening screen is employed. The oversize is stock-piled or sold for ballast.

Undersize is presented, by bucket elevator, to a series of three magnetic rolls. Advantage is here taken of the variation in degree of magnetic susceptibility among coke, sinter, and low-zinc, high-iron residue. The top roll removes the high-iron, strongly magnetic material; the middle roll removes a product somewhat higher in zinc and lower in iron than the "lo zinc" of the first roll. The third roll removes a "hi zinc" product, which is returned in

part to the raw mix for the sinter machines. The nonmagnetic product consists of coke and sinter. This mixture passes in a free-falling stream through an air separator, in which the reclaim coke is blown away by air blast from the heavier reclaim sinter.

Over a period of time, it is necessary to discard as much iron in the residues as enters the smelter circuit in the concentrates. This iron balance is secured by varying the magnetic flux density of the first and second rolls and is assisted by screening the product of the third roll ("hi zinc") to discard a portion of the oversize (+0.171-in.) and return a portion of the undersize, minor in amount, to the sinter circuit.

Reclaimed sinter joins new sinter sent to the furnace feed bins (or, alternatively, is returned to the sinter raw-mix circuit) and amounts to 3 to 10 per cent of the total weight of sinter. Reclaimed coke joins the new sized coke and amounts to 35 to 45 per cent of the total coke used. The reclaim coke and reclaim sinter are screened at 0.171 in. to remove the product called "residue fines," which is returned to the sinter circuit.

Composition and weight distribution of residue components is shown in Table 3.

TABLE 3.—*Average Composition and Weight Distribution of Residue Components for the Year 1942*

Material	Total Wt. of Residues, Per Cent	Zn, Per Cent	Fe, Per Cent	Per Cent C, Approx.
Reclaim sinter....	5	25.7	14.3	18
Reclaim coke.....	40	10.7	8.7	54
Residue fines.....	9	22.3	12.0	24
Hi-zinc.....	3	15.4	21.7	10
Lo-zinc.....	13	10.0	37.2	5
Oversize discard..	30	11.6	24.5	8

Blue powder is worked up in another section of the residue plant. Water from the condenser-gas washer is passed through a

series of settling ponds, which have concrete sides and earth bottoms. Settled solids are removed periodically by loco-

belt conveyor discharging into a 70-in. dia. by 50-ft. long countercurrent, direct coal-fired rotary drier. Dried material, more or

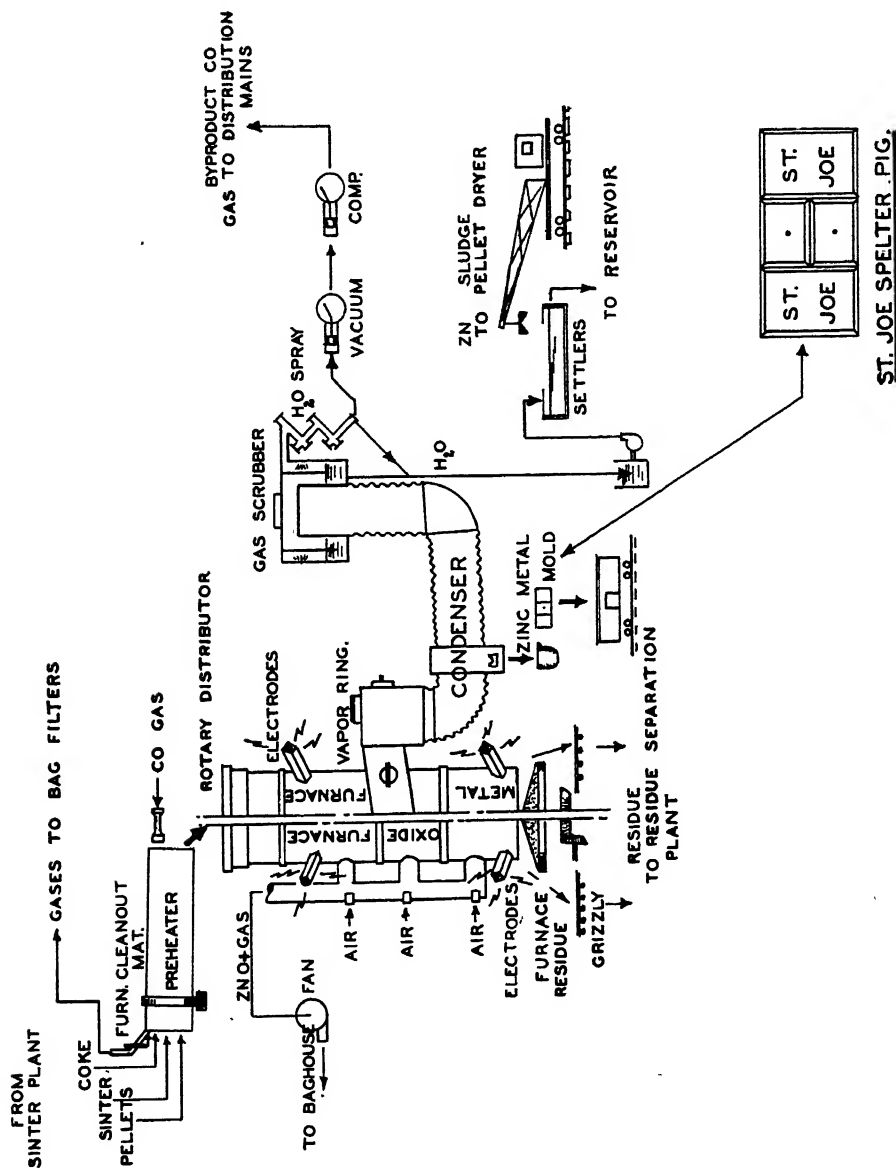


FIG. 6.—FLOWSHEET OF FURNACE PLANT.

tive crane and clamshell and stock-piled at the end of the pond chain adjacent to the residue plant. A gasoline-driven truck-tractor scoop feeds stock-piled material to a

less pelletized, is pan-conveyed to feed bins above each furnace. Material withdrawn from these bins joins the sinter and coke entering the furnace preheater.

Electric Furnace

The essential features of operation of the electric furnace are weighing out required proportions and amounts per unit time of sinter and coke, preheating these materials, distributing the preheated feed in the upper part of the furnace shaft, transformation of electrical energy to its thermal manifestation by passage through the charge, reaction between carbon and oxidic zinc materials to form carbon monoxide and zinc vapor, withdrawal of these gases from the furnace followed either by burning to oxide or condensation to metal, discharge of residues from the bottom of the furnace shaft.

The furnaces are cylindrical shafts closed at the top by the horizontal rotating charge feeder-distributor and at the bottom by a convex rotating table. One group of electrodes protrudes through the furnace wall near the top of the shaft and another group is located near the bottom. Reaction products—zinc vapor and carbon monoxide—are removed in a manner described in the following pages.

Mixture of feed for the furnace is approximately one volume of coke to one of sinter, a typical charge to a 69-in. dia. furnace being 43 lb. sinter and 19 lb. coke per minute. The large excess of coke in respect to that stoichiometrically equivalent to the reducibles present provides electrical stability and possibly also tends to minimize agglomeration of charge constituents heated to near melting temperature in the furnace.

Preheated charge is laid down in the furnace in a particular manner, by a distributor disk and spout rotating horizontally around the axis of the furnace. The rotary distributor is also the closure for the top of the furnace shaft, a seal being provided by a skirt immersed in a ring of sand. The distributor spout is so positioned as to lay the charge down in an annulus relatively closer to the wall of the shaft

than to the center. The resulting concavity, diminishing outwardly from the axis, permits the larger particles, particularly coke, to roll toward the center. The result of this controlled size segregation is a maximum of electrical conductivity along the shaft axis and lessened conductivity toward the furnace walls. Over-all electrical resistance is in major part a function of the number of contact resistances in the path of the current, other considerations, such as temperature, being equal. The current distribution control, as described above, is implemented by making the coke larger than the sinter. The size specifications are:

Size	Coke, Per Cent	Sinter, Per Cent
$-\frac{3}{8} + \frac{3}{8}$ -in.	76	56
$-\frac{3}{8} + \frac{1}{4}$ -in.	19	39
$-\frac{1}{4}$ -in.	5	5

Since the average particle size of the coke shrinks during passage through the furnace, the new sized coke is made about 86 per cent $+\frac{3}{8}$ -in., in order that the mixture with reclaimed coke may possess the size distribution specified. Sinter size is controlled, as mentioned earlier, by mixing two sizes of sinter and also, in the broader aspect, by adjusting the silica content of the sinter.

Temperatures in the furnace follow the pattern of distribution of electricity, being hottest along the center line of the furnace. A primitive but quick and effective means of ascertaining temperature distribution consists in poking a steel bar horizontally through the charge and allowing a period of residence sufficient to develop the color effects of temperature differences on the bar, so that the zones may be seen and measured when the bar is withdrawn from the charge. Such an operation is vernacularly referred to as "taking a core." Cores are usually taken at 120° spacings and at one or more levels, six times daily. Temperature distribution

is approximately 900°C. near the wall, 1200°C. in the main body of charge, graduating to 1300° to 1400°C. at the center.

Electric power is limited to 475 to 500 kw. per electrode circuit, as heavier loadings lead to a disproportionate increase in consumption of the electrode tip. Gross consumption of electrodes 12 in. square by 72 in. long is 4 to 5 lb. per ton of zinc equivalent produced. Net consumption is perhaps 60 per cent of this. It has not been found economical to join butts to new electrodes in the manner familiar to arc-furnace operations employing round electrodes. The electrodes are sloped downward 30° from the horizontal and are set "diamond-wise," so as to provide the least possible impediment to the downward flow of coke and sinter particles. Insertion depth is 11 in. for the upper electrodes and 8 in. for the lower set. The position of the latter is not critical, because usually embedded in a ring of electrically conducting slag, and is adjusted only infrequently. The upper electrodes wear away about an inch a day and are repositioned every 5 to 7 days. Electrode apertures, originally close fitting, are now of generous proportions and are easily and effectively sealed by balls of moistened short-fiber asbestos.

Power is controlled automatically by an electronic device of local design, actuated by the individual circuit wattmeters, which adjusts the voltage regulators. Voltage drop across the furnace varies widely, being high after power has been off for a period—as, for example, during a vapor-ring clean-out—and falling to a lower value after thermal equilibrium has been reestablished. The working range is usually 260 to 160 volts with 1800 to 2700 amp. per circuit.

Furnace power is delivered to the electrode clamps by a ¼ by 6-in. copper bus, 2500 amp. being the design loading. Busses are interlaced from the transformers to the furnace but are necessarily separated by the 26 ft. intervening between the upper

and lower electrode sets. Power factor of the furnace proper is essentially unity. Over-all power factor of transformers, bus system and furnaces is something over 95 per cent for the small furnaces and 90 to 95 per cent for the large furnaces, where there is of necessity further separation of the conductors. Load factor is high, of course.

Of the total power billed, about 20 to 23 per cent is distributed to points of consumption (i.e., acid plant, charge-preparation equipment, offices, shops) other than electric furnaces. For 1942 and 1943, the ratio of total power to production was 3258 kw-hr. per ton of zinc equivalent produced. Direct furnace power was 2554 kw-hr. per ton of zinc equivalent.

In the metal-producing furnaces the furnace reaction products are withdrawn through vapor ports located in a circle a distance below the upper set of electrodes, roughly one third the space between the two sets. The circle of vapor ports is surrounded by an annulus called a "vapor ring," which leads to the condenser. The construction and operation of the condenser are described by one of the co-inventors, H. K. Najarian (p. 161, this volume).

In the oxide process, reaction products flow through tewels distributed in the furnace wall between the upper and lower electrode sets. Each vertical line of tewels communicates with an oxidation manifold, which in turn joins a duct leading to fan and baghouse. Combustion is controlled by the amount of air admitted at the tewel exit. In general, low-temperature combustion produces oxide particles of smaller size than are produced in a combustion zone of higher temperature. Particle shape in part is a function of combustion velocity.

Refractories play an important role in the economics of any furnace process and electrothermic zinc furnaces are no exception. The furnace shaft is built up of a series of short ring sections, each supported on its own skewback. By this for-

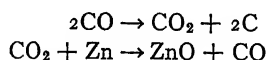
tunate arrangement, one portion of the furnace can be torn out and renewed without disturbing other parts. Since furnace campaigns terminated by operating difficulties are almost invariably either directly or indirectly attributable to the refractories of either the furnace or the condenser, an active test program of new methods and materials of construction has been carried out since the beginning of operations. Some rather interesting developments have been made, particularly in the use of structural carbon.

For the most part the furnace shaft is laid up with 13 by 3-in. key brick of low alumina content (Walsh S)⁶ and of as low a porosity and permeability as it is possible for the suppliers to make. The underside of the rotary distributor is lined with bonded silicon carbide (Carbofrax D) shapes. The roof of the vapor ring posed an interesting construction problem, solved by a self-supporting flat arch of Carbofrax. Condenser and vapor conduit are lined with Carbofrax D. Cast mullite blocks are extensively used as an inner lining below the vapor ring. The bottom of the furnace shaft is supported on a hollow water-cooled ring.

Structural carbon is a remarkable and at the same time a tantalizing material. Its low coefficient of expansion, high coefficient of thermal conductivity, and relatively enormous strength at high temperatures are valuable properties, but are only to be taken advantage of after consideration of and provision for the following facts: It must be kept out of contact with air and carbon dioxide; it must not be allowed to serve as reduction carbon for reducible oxides in the furnace charge; it must be so located as not to interfere with the desired distribution of electricity through the furnace.

One of the more conspicuous successes has been the use of carbon beams for vapor-port lintels. These beams not only eliminated the terminal effects of wall gutting,

an erosive action that merely ignored and went around water-cooled inserts, but transmitted sufficient extra heat to the vapor ring to substantially minimize the reverse reactions,



which are the principal cause of rock oxide formation.

Refractory consumption in 1941, the latest year for which ratios have been established, was as follows:

Oxide furnaces: firebrick and mortar, 33.6 lb. per ton of zinc equivalent produced.

Metal furnaces: firebrick and mortar, 53.5 lb. per ton of zinc produced; silicon carbide, 4.2 lb. per ton of zinc produced.

Because of longer furnace campaigns, the present consumption ratio is known to be lower. The average campaign length for all metal furnaces shows the following trend: 1940, 64.4 days; 1941, 62.3 days; 1942, 86.3 days; 1943, 98.5 days. Oxide furnaces exhibit a campaign life of the order of 250 to 300 days or longer. Repair period between campaigns ranges from 10 to 15 days, depending on extent of repairs required.

TABLE 4.—*Production Statistics*

	Small metal furnaces	Large metal furnace	Small oxide furnaces	Large oxide furnace
Tons feed per day.....	50.6	86.7	48.9	76.1
Tons Zn equivalent produced per day....	17.0	25.2	15.7	24.3
Per cent Zn in feed.....	43.9	42.7	42.8	42.5
One-pass recovery, per cent.....	76.5	67.9	74.9	75.0
Tons feed per ton Zn in product.....	2.98	3.45	3.12	3.13
Zn produced, kw-hr. per lb.....	1.266	1.321	1.264	1.291
Approximate per cent Zn in residues.....	14.6	15.3	16.5	15.4

Production per furnace has increased since the earlier papers were written. It is not uncommon for the small furnaces to produce upward of 20 tons of zinc a day.

Because of vapor-ring cleanouts, electrode changes, distributor top changes, and other changes, the average daily production is

per cent, zinc in products divided by zinc in raw material, for the 160,000 tons of zinc equivalent produced during the three-

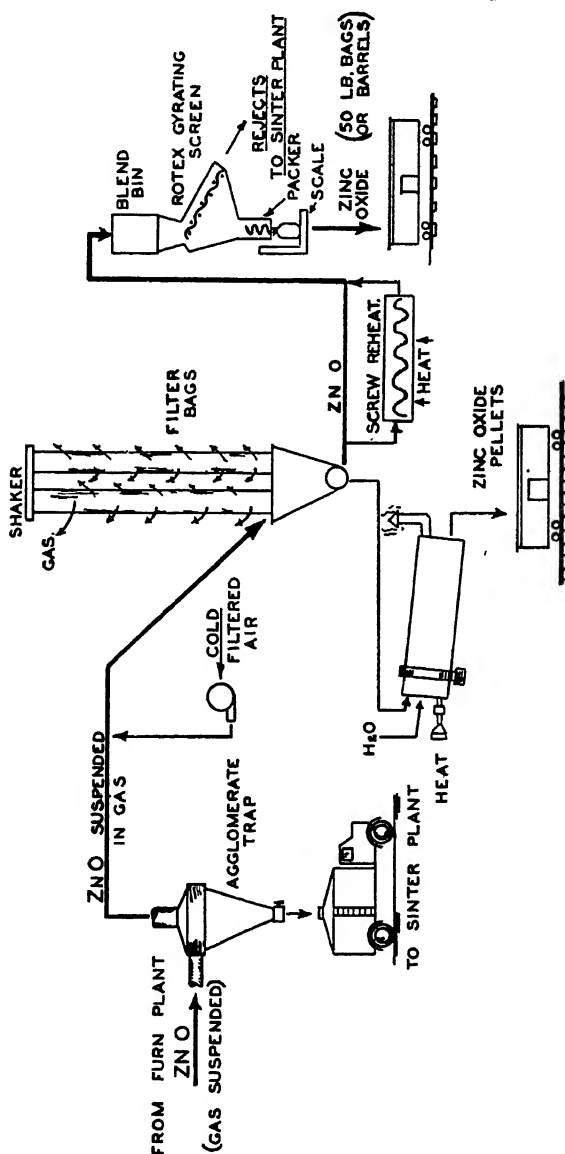


FIG. 7.—BAGHOUSE COLLECTION OF ZINC OXIDE.

somewhat lower. Some statistics for the period 1942-1943 are given in Table 4.

As noted previously, a portion of the residues are sorted out and returned, resulting in an over-all smelter recovery of 89.7

year period of 1941, 1942, 1943. This recovery ratio was substantially higher (by about 4 per cent) before the advent of lower grade concentrates and higher driving rates.

Principal production interrupting service maneuvers that must be carried out during a furnace campaign are electrode changes, top changes, and, for the metal furnaces, vapor-ring cleanouts. Electrode adjustment requires about 40 min. every fifth or sixth day. Rotary distributor-top changes require 20 min. every three to four weeks. Vapor-ring cleanouts take about 100 min. every third day. During the latter maneuver, furnace charge that has rolled through the vapor ports is hoed out of the vapor ring, and any accumulations are chiseled out. A motor-driven auger effectively bores out the vapor conduit leading downward into the condenser.

An interesting operation, that of "bombing" the vapor ring, is conducted without interrupting the power, furnace feed or condenser-gas flow. The purpose of bombing is to counteract the diminution of effective orifice area in the charge lying in and adjacent to the vapor-outlet ports. The interstices tend to filter out dust particles swept along by the gaseous reduction products. After a period of 4 to 6 hr. the resistance to gas flow becomes appreciable (1 to 3 in. H_2O). This is relieved by introducing into each vapor port a bomb consisting of an 11-in. length of 1-in. standard-weight iron pipe containing 8 in. of water and sealed (by double bead welding) at each end. The temperature in the vapor-port charge accumulation (900° to $1200^{\circ}C.$) is sufficient to explode the bomb in one to two minutes.

Zinc Oxide Plant

Products of combustion of the zinc vapor and carbon monoxide issuing from the furnace tiewels are transferred by fan and ducts to the baghouse. Filter area provided is about 14 sq. ft. per pound of gas filtered each minute. Gas temperature at entrance to bags varies considerably, with 275° to $300^{\circ}F.$ as maxima. Bag pressure is of the order of 1-1½ in. of water. Bags are shaken

in groups of 50 for 2 min. out of each 30 min. During the shaking period the 50-bag unit is dampered off by solenoid valve controlling an air cylinder.

Shake-out oxide falls into the screw-conveyor elevator system leading to the collect bins. A series of adjustable-speed cross screws permits blending of material withdrawn from different bins. Blended material passes through a shaking screen (Rotex) to break up any soft agglomerates and thence to an auger compressing packer. Fifty-pound bags are standard. Export shipments usually go in wooden barrels.

A number of different grades of oxide are produced, varying chiefly in physical properties as affected by particle size, size range, distribution of sizes and particle shape. One aspect of particle-size control, combustion temperature, has already been mentioned. Compression of size range is accomplished by taking advantage of the fact that surface energy (hence vapor pressure) varies inversely as the radius of curvature of the particles. The smaller particles of a low-combustion-temperature oxide have an equivalent diameter of the order of 100 Ångstrom units. Important new information—substantiating J. J. Rankin's earlier findings with the light microscope—concerning spatial properties of pigments, is being developed with the aid of the electron microscope by a company-supported fellowship.

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Weaton-Najarian Vacuum Condenser

By H. K. NAJARIAN,* MEMBER A.I.M.E.

THIS paper is a companion piece to the description of the electrothermic process that begins on page 141. It will be confined to a brief story of the development of the Weaton-Najarian vacuum condenser† at this plant, together with up-to-date design and operating data.

The Josephtown smelter was designed primarily for production of zinc oxide. However, the development of a method for production of zinc metal had always been under consideration, and accordingly one of the original eight units of the electrothermic furnaces built in 1930 was set up to produce metal. The design of this furnace was identical with that of the oxide furnaces except that in place of oxide teewels opening into oxide manifolds, conventional conical clay condensers—similar to condensers used in horizontal retort smelting—were installed around the periphery of the furnace and in several tiers vertically for condensing the zinc vapors.

The early experimental work in trying to condense zinc out of the mixtures of zinc vapor and carbon monoxide gas from the electrothermic furnaces indicated that, while the gases from electrothermic smelting would condense in surface-type condensers, the formation of blue powder was excessive and condenser efficiency low. Furthermore, operating a large unit of electric furnace with several hundred small condensers, with attendant high labor cost and unfavorable operating

conditions, did not appeal to us. We also realized that a single unit of surface condenser capable of condensing 12 to 15 tons of metal per day would be of huge dimensions and possibly difficult of control. So we took as our aim the development of a method whereby a single condenser unit of reasonable dimensions would condense zinc, in one step, from the large volume of gases that the electric furnaces produced. We set about searching for knowledge on zinc metallurgy and design of zinc condensers in particular.

Our study of the prior art focused our attention on the oft-repeated statement by earlier experimenters, that the most efficient way to condense metallic vapors, such as zinc vapors, was to bring the vapors into "intimate contact" with molten metal; but the methods offered for securing this "intimate contact" in any practical manner left much to the imagination. We were handicapped by not having someone on the Josephtown smelter staff who could lay claim to being an expert zinc metallurgist and could give guidance from actual experience on the practicability of various schemes that haunted our imagination.

LABORATORY EXPERIMENTS

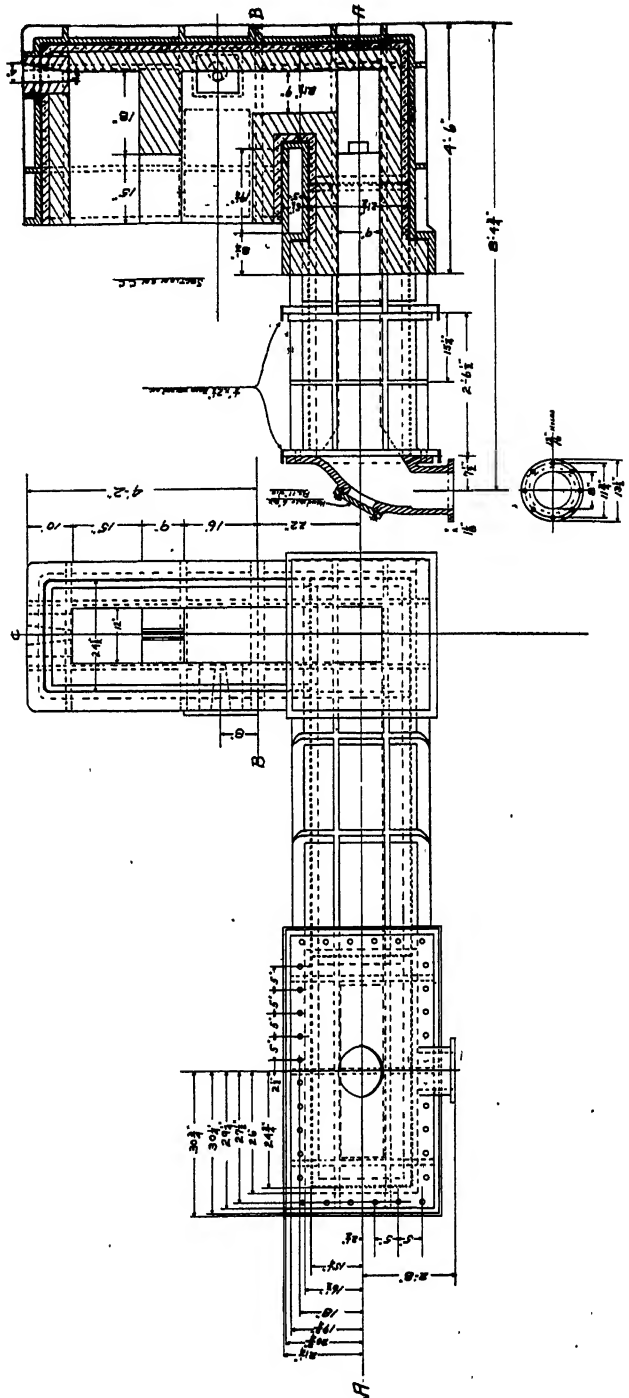
However, we had an expert ex-steam engineer in the person of George F. Weaton, manager of the Josephtown smelter, who had had long experience with steam-jet condensers and would reiterate his belief at every opportunity that the logical and the most efficient way to condense zinc would be with a jet-type condenser. We became intrigued by the possibilities of a zinc con-

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† U. S. Patent 2070101 (Feb. 9, 1937).

WEATON-NAJARIAN VACUUM CONDENSER



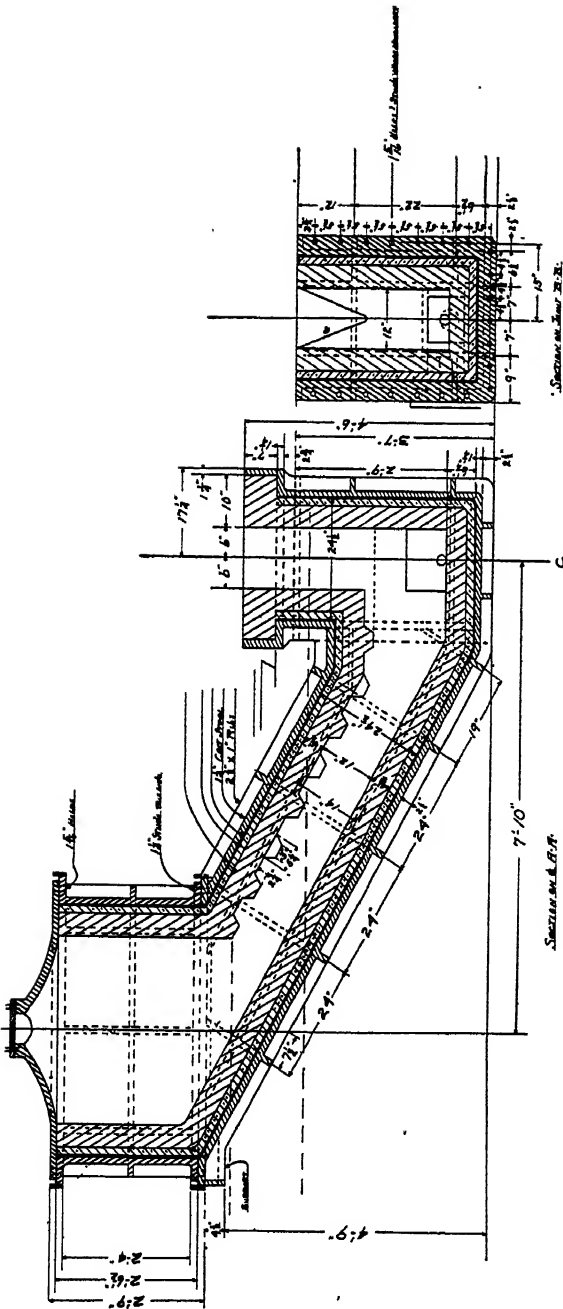


FIG. 1.—DESIGN OF FIRST EXPERIMENTAL CONDENSER.

denser designed on the principle of a steam-jet condenser, where the heat of condensation would be dissipated by circulating the molten metal through a heat exchanger.

We could conceive of no apparatus built of commonly used materials of construction that, in a practical way, could be made to receive condensable furnace gases at around 850°C. and compress the gases to a pressure sufficiently high to permit injection into a bath of molten zinc. At this point, "horse sense" came to the rescue; if it were not practicable to inject the gases into the bath of molten zinc by pressure, why not bubble the gases through the molten zinc by suction? This would probably be the nearest approach to steam-jet condenser conditions we could hope to attain, and nothing could be simpler, for this purpose, than a U-tube. It would permit easy cooling by external application of cooling medium, while handling of cooler uncondensable gases by a gas exhauster would be relatively simple.

Following this "hunch," we charged several pounds of zinc sinter in a small laboratory retort, together with sufficient granular coke, and attached one leg of a U-tube made of 2-in. steel pipe to the mouth of the retort. The vertical legs of the U-tube were about 12 in. high, the bottom connecting piece about 12 in. long and inclined about 15° from the horizontal. When the charge in the retort began to smelt and zinc vapors rose through the peep-holes in good volume, molten zinc was poured into the U-tube, completely filling the bottom inclined portion. The outgoing leg of the U-tube was attached to a pipe leading to a small vacuum pump. Shortly after the vacuum pump was started, a match was applied to the exhaust of the vacuum pump and to our delight the gas burned with the characteristic blue flame of the CO gas, with occasional puffs of zinc oxide fume.

After about 15 min., the U-tube became hotter, indicating that some zinc vapors

were condensing in the molten zinc. After about 90 min. of operation, molten zinc began to trickle out of a hole eaten through the bottom of the steel pipe, and this stopped the experiment.

EXPERIMENTS OF PILOT-PLANT SIZE

The pipe connecting the U-tube to the vacuum pump showed only a light coating of blue powder. We began to suspect that we were on the right track. Therefore, a condenser of pilot-plant size was designed and built, large enough to hold about a ton of molten metal (Figs. 1 and 2). It consisted of a cast steel shell of rectangular cross section, lined with silicon carbide brick with a lining of 3/4-in. thick asbestos plank between the steel shell and the brick lining, to protect the steel shell from molten zinc that might leak through the brick joints. The condenser was roughly a U-tube with a short, vertical gas-inlet leg, main condenser section set at 30° from the horizontal and a vertical outlet chamber terminating in a flanged round hole from which a pipe ran to a vacuum pump placed some distance away. The inlet end of the condensing chamber at its lowest point opened at the bottom into a forehearth, or tapping well, set at right angles. The forehearth had two compartments, separated by a brick baffle compartment, the one next to the condensing chamber acting as a metal seal and the other compartment catching the overflow of metal from the condenser well. The roof of the condensing chamber on the inside was provided with brick baffles projecting downward to impede and break up the gas bubbles, and to prevent gas going through the metal intermittently in large bubbles.

The slope of the condensing chamber in this experimental unit and several of the subsequent commercial units was set at 30° from the horizontal, after study, with glass-front models, of the behavior of air bubbles being sucked through a bath of

water or mercury in a vessel simulating the design of the condenser. We found that at 30° slope the air bubbles broke up finer and agitation was more thorough and flow of gas more uniform than with slopes under or over 30°.

This experimental condenser was attached to one of the tiewels of an oxide furnace, with a damper between the furnace and the inlet leg of the condenser. After preliminary heating of the condenser, and priming with molten metal, the condenser was opened to the furnace and vacuum applied on the exit leg. We could hear the gas bubbling through the metal and soon the temperature began to rise, and the condenser became excessively hot, as we had no means of cooling the shell except by natural air circulation. After some six hours of operation, bubbling slowed down and soon stopped completely. After the metal was tapped out and the condenser allowed to cool, examination disclosed that the exit pipe and part of the piping to the vacuum pump were almost completely plugged with metal splash from the condenser and with blue powder.

From a number of runs of short duration made with this small condenser, we learned:

1. When zinc vapors are bubbled through a bath of molten zinc and the temperature of the zinc bath is kept relatively low (around 500° to 525°C.), rapid and almost complete condensation of zinc vapors can be obtained, irrespective of the amount of accompanying noncondensable gases. The phenomenon may be similar to the formation of rain droplets from water vapors when brought suddenly below the dew point under favorable temperature and pressure conditions. In our experiments, the minute droplets of metal formed by sudden chilling, being surrounded by molten metal, were transformed into coherent metal.

2. Construction of the condenser walls must permit efficient heat exchange, so that large amounts of heat of condensation

evolved (roughly 1000 B.t.u. per pound of metal condensed) may be dissipated by application of a cooling medium such as water or air to the outside surface of the



FIG. 2.—FIRST EXPERIMENTAL VACUUM CONDENSER.

condenser chamber in the regions enclosing the molten metal charge.

3. The exit leg of the condenser must be much higher than the other, and baffled to prevent metal splash from reaching the exit piping.

4. Gastight access doors must be provided for the gas inlet (downleg) and the gas passage from the furnace, to permit periodic cleaning of the inlet passages of accretions of rock oxide.

5. There must be an apparatus for washing the exit gas from the condenser, to prevent blue powder from plugging the vacuum piping and the vacuum pumps.

CONDENSER OF COMMERCIAL SIZE

We now designed and built our first commercial size condenser, figured to handle the entire production from one of the 57-in. bore furnaces, 10 to 12 tons of metal per day. This condenser (Fig. 3) had a cast steel shell, ovate in cross section throughout the length of the condensing

chamber, set at 30° slope, with both gas inlet and outlet legs circular.

It was lined with specially designed 2-in. thick silicon carbide brick, with three

then downward through a water-sprayed annular chamber, then up again through the outer water-sprayed annular chamber and thence to the vacuum pumps. The

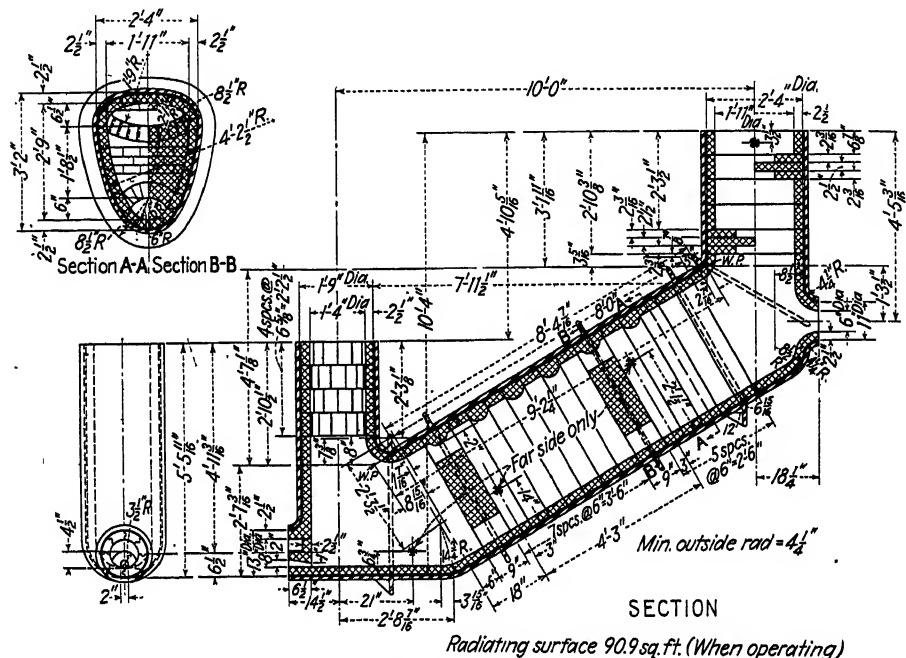


FIG. 3.—FIRST COMMERCIAL CONDENSER.

$\frac{1}{32}$ -in. thicknesses of overlapping phlogopite mica sheets between the brick and the shell. Ovate cross section was adopted, with a wide, flat arch top, with the thought that the gas bubbles would spread out over a larger area in their passage through the condenser, and also that there would be more efficient cooling by water sprays on top of the condensing chamber, the point of maximum heat generation. Brickwork was revised in one of the furnaces to provide a single vapor passage through an annulus (vapor ring) to the condenser.

Gastight access doors were provided for all vapor passages and both ends of the condensing chamber. A gas washer was installed on top of the gas-outlet leg, which permitted the gas to enter the washer through a central pipe from the bottom,

vacuum control valve was at the gas outlet from the washer.

An innovation on this condenser was a continuous metal discharge. Instead of a metal well attached to the lower end of the condenser, there was a metal overflow weir at the gas-outlet end of the condensing chamber. This kept the metal level at a constant height during operation, the excess metal, as made, flowing down through a refractory-lined (inside and outside) steel tube into a separate deep metal pot, to provide seal against the vacuum in the discharge leg of the condenser. The idea was to operate with a constant vacuum and constant zinc level, let the metal overflow into the pot as made, and tap the metal from the pot. However, it proved very difficult to keep the metal

discharge tube open. It would plug up every few hours with dross and fine coke and sinter that floated on top of the metal in the condenser and worked down the tube, and also with dross caused by leakage through the lining of the overflow tube. Therefore, after several runs of short duration, the scheme was abandoned and a tapping well was installed near the lower end of the condenser, opening into the bottom of the metal bath in the condenser. The design of this simple tapping well proved practical and has been used ever since (Fig. 6).

The condenser was water-cooled by sprays applied on the top and two sides of the part of the condenser shell that surrounded the metal bath, and wetting the entire periphery.

An unsuccessful search was made for a metal or alloy that would not be attacked by molten zinc at temperatures near its boiling point. Tungsten was the only metal among many alloys and metals tried that would not actively dissolve in molten zinc. Our thought was that if we could make the condenser wall of a material resistant to action of molten zinc, and with a much higher heat conductivity (an alloy steel, for example) than our condenser wall, made of outer steel shell, mica interlining and silicon carbide inner lining, we could build large-capacity condensers with comparatively small dimensions and also save some of the cost of construction and maintenance. However, the brick-lined condenser wall has one advantage over a metal wall, in that it enables us to keep the metal in the condenser molten during 2 to 3-hr. shutdowns for periodic furnace and condenser cleanouts without resorting to external heating of the condenser. In actual practice, water sprays are shut off prior to a cleanout period and the condenser temperature is allowed to rise above the normal, to allow some margin of safety.

Gradually, as we progressed in operating technique, we were able to make longer

campaigns with our metal furnace and condenser. Additional furnaces were set up for metal production. To get greater capacity out of the furnaces, the bore was increased to 69-in. diameter, which in turn necessitated increase in the condenser capacity. Since the dissipation of the heat of condensation is the main factor affecting the condensing capacity, the logical thing appeared to be to increase the length of the condenser, but vacuum that could be maintained in the condenser was limited to about 18 in. of mercury for practical operating conditions, roughly corresponding to 36 in. head of zinc metal in the condenser.

It was evident that we could not lengthen the condenser and still maintain the 30° slope, which we had found to give optimum results. Therefore, we built the next condenser with the condensing chamber at 30° for the first half of the length and the remainder horizontal. While increased cooling area was secured, relatively small variations of the metal level in the horizontal section, from periodic tapping and consequent lowering of the metal level, made bubbling more irregular, and increase in cooling effect in proportion to the increase in cooling area was not realized. Therefore, all later condensers were made long enough to give the desired volume and cooling area and with less slope, the slope being determined for each length of condenser to secure a metal-level differential during normal operation of about 28 to 36 in., roughly corresponding to an operating vacuum of 14 to 18 in. Hg.

The cast steel shell of the first few condensers proved troublesome, in that frequent cracks would develop during operation, mainly from progressive expansion of refractory lining and also possibly from initial strain developed from welding several sections of the shell together during construction. Cracks at the top and sides of the shell would be repaired by stopping the operation, spot-freezing the zinc leak-

age by a stream of water, quickly cleaning the break, packing it with mortar and welding the crack. On several occasions cracks occurred at the bottom of the shell and metal came out in such quantity that it was impossible to freeze; a large amount of metal ran over the floor and filled the water troughs under the condenser before the condenser could be tapped out.

A rolled steel shell was adopted, having a circular cross section and corrugated throughout the main part of the condensing chamber and part of the upleg, to provide for expansion. The brick for the lining was redesigned to fit the corrugated shell in rings. This design is now standard on all condensers. Although the corrugated shell design has not eliminated cracking of the steel shell, it has almost eliminated shutdowns caused by the cracking, as repairs on the shell are now usually of a minor nature and can be done mostly during cleanout periods.

Early in the development work, it was necessary to remedy the violent periodic vibrations caused by sloshing of heavy molten metal in the condenser. This "water-hammer" effect was probably the cause of some refractory failures and cracking of the cast steel shell. This hammer effect was reduced to harmless proportions by brick dams submerged in the metal bath. The dams are keyed securely to the brick lining of the condenser and have two arched openings, one on top and one at the bottom, to permit movement of gases toward the discharge end of the condenser and for sloshing of metal back and forth, though in a much more subdued fashion.

POSITION OF CONDENSER IN GENERAL SCHEME

The position that the condenser and its auxiliaries occupy in the Josephtown electrothermic metal-producing units is illustrated in the schematic diagram of Fig. 4. The furnace reaction products, comprising

roughly 45 per cent zinc vapor and 55 per cent CO gas, are drawn from the furnace through the vapor ports, then through the "vapor ring," through a connecting outlet, down the vertical gas-inlet leg of the condenser and through the metal bath by the action of vacuum maintained over the metal bath in the gas-outlet leg of the condenser. The CO gas, together with uncondensed portions of the zinc vapors, pass first through the gas washer, provided with water sprays, which cool the gases and wash most of the larger particles of coke and sinter dust and blue powder. The gases then pass through a Long-Deeley deduster, consisting of a series of pipes with several right-angle turns in each run and with a steam jet at the entrance and water spray at each right-angle turn. The deduster washes the very fine particles of dust escaping the water sprays. The spray water from the washer and deduster finds its way through separate pipes down into a sump tank. The ends of the pipes are immersed in the sump water, to provide a barometric seal against the vacuum in the system. The wash water from the sump is pumped to ponds for settling of blue powder.

The gas from the deduster passes through a motorized vacuum control valve, enters the vacuum header pipe and joins the gas coming from other condensers. Reciprocating vacuum pumps maintain a vacuum of about 22 in. in the vacuum header in the furnace plant. The CO gas from the vacuum pumps is led through a water-cooled heat exchanger, a gas filter and thence to compressors, which deliver the gas to plant CO gas mains under 30 lb. pressure. Provision is made against danger of compressors pulling outside air into CO gas stream by a "barometric leg," one leg of which ends in a water seal, thus, while preventing ingress of air if vacuum conditions prevail at the inlet of the compressors, will permit exhaust of CO gas through the seal if compressor capacity is insufficient at

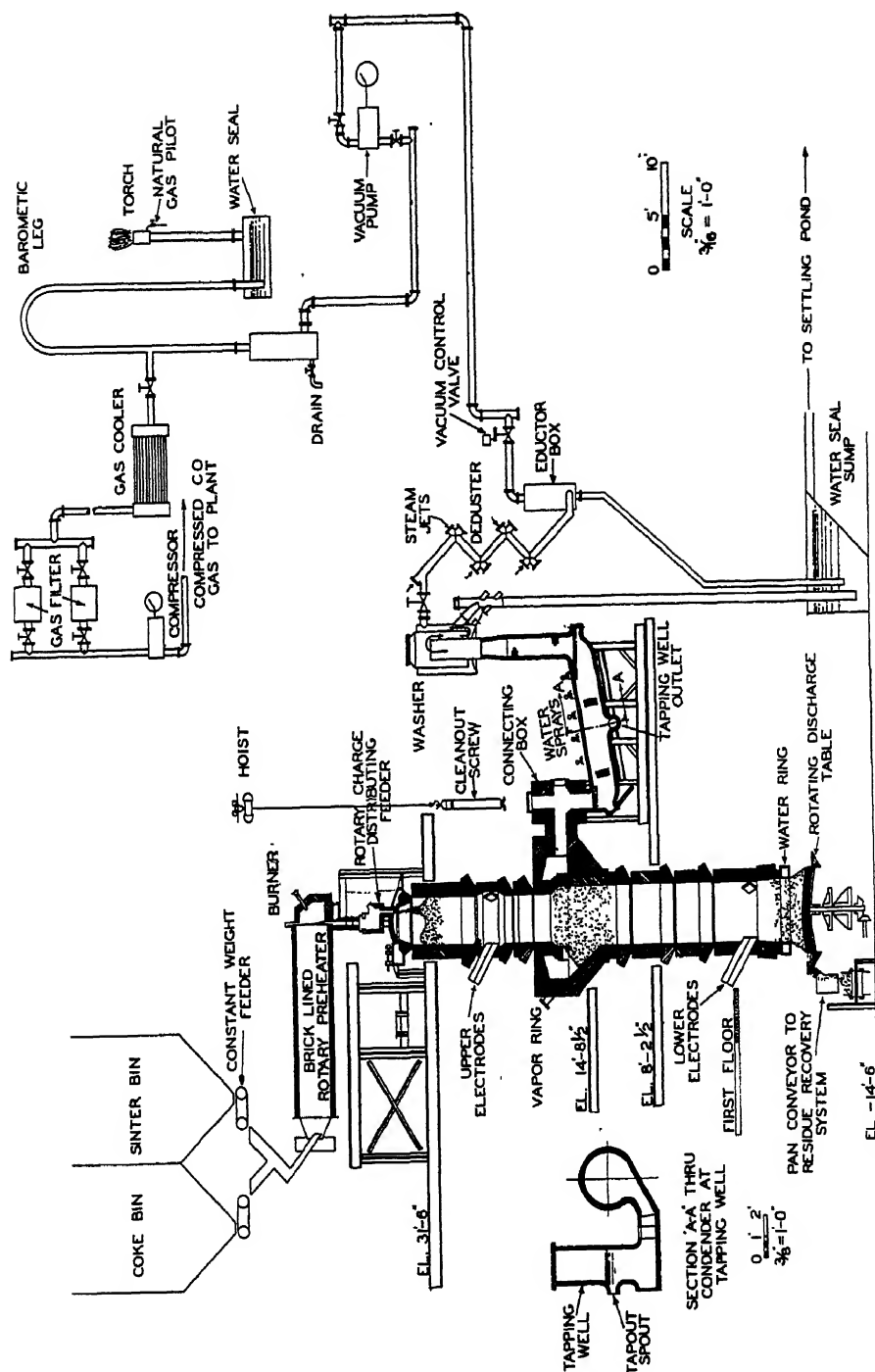


FIG. 4.—FURNACE, CONDENSER AND AUXILIARIES.

any time to handle the gas discharge from the vacuum pumps. This excess CO gas automatically is discharged to a torch with a natural-gas pilot and is burned in the open.

lining is allowed to dry somewhat before the brick are laid.

Carbofrax D carborundum brick is used for the inner lining, all special shapes, hard pressed to make it as impervious to molten



FIG. 5.—31-FOOT VACUUM CONDENSER ON 96-INCH BORE FURNACE.

Vacuum pump capacity required is on the order of 90 cu. ft. of free air capacity per ton of metal per day.

PRESENT DESIGN

Design of the condenser proper in its present state of development is shown in Fig. 6. The outer shell is $\frac{5}{8}$ -in. thick boiler plate, and sections subject to appreciable linear expansion are made corrugated similar to Scotch Marine boiler of the Morrison furnace. The mica interlining is applied to the inside surface of the shell in sections preparatory to the laying of the brick lining. The built-up phlogopite mica comes in 36-in. square sheets, $\frac{1}{8}$ in. thick, unpressed and undried and in sealed containers, to prevent drying of the binder. It is pliable enough to permit fitting to the contour of corrugations and elbows and is glued in place with water glass. The mica

zinc as possible (about 14 per cent porosity). Thickness of the carborundum brick at the elbows and all uncorrugated parts is 2 in. At corrugated sections the brick is made one corrugation wide, back to fit the corrugation, 2 in. thick at the two edges forming the ring joints, interlocked and keyed along the circumference. The baffles are also carborundum brick and made of special shapes to permit each course to be keyed in place.

Vacuum-tight doors permit access to the inside of the condenser for repairs, for tapping out the metal, and for removing accretions during cleanouts. The short gas-inlet leg of the condenser is attached to the bottom side of the vapor ring connecting the box with a gastight door directly on top of the inlet leg, to permit cleaning of accretions accumulating in the inlet leg; also with another door directly in front of

the passageway from the vapor ring to the connecting box.

As the inlet leg of the condenser is supported from the furnace connecting box

performance data under varying operating conditions.

Fig. 7 shows the relation between zinc production rate and condenser temperature

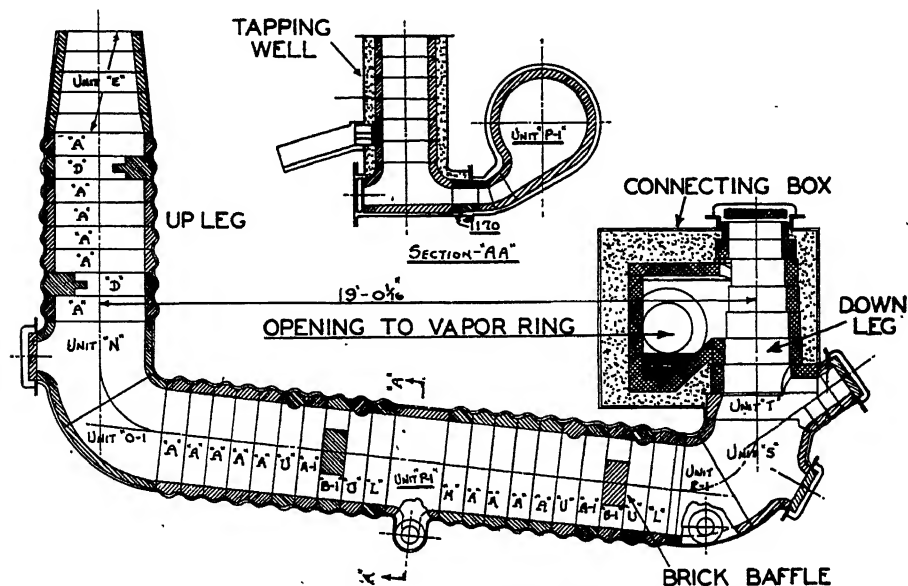


FIG. 6.—22-FOOT CONDENSER.

and fixed, to provide for expansion, the condenser is supported at the other end, under the upleg, on rollers, the upleg and the washer being free to move. At intermediate points the condenser is also supported by hangers that allow longitudinal movement of the condenser.

The length of the condenser on a 96-in. bore furnace is roughly 31 ft. over all. The length of the condenser on the remaining five units of 69-in. bore furnaces is 22 ft. The diameter measured inside the brick lining is 32 in. The wetted area in the 31-ft. condenser is about 250 sq. ft. under normal zinc loading; that of the 22-ft. condenser is about 170 sq. ft. Coefficient of heat transmission through the condenser shell, consisting of $\frac{5}{8}$ -in. outer steel shell, three layers of $\frac{1}{32}$ -in. mica and 2-in. Carbofrax D brick, varies from 6.0 to 8.0 B.t.u. per hour per square foot of wetted area per degree Fahrenheit, determined from actual

for various values of over-all heat-transfer coefficients. Fig. 8 shows the relation between condenser temperature and over-all heat-transfer coefficient for various gas compositions and gas temperatures. Fig. 9 shows the relation of over-all heat-transfer coefficient to zinc loss from the condenser (blue powder).

Table 1 gives the vapor pressure of zinc and theoretical uncondensed zinc vapor in outlet gases for various condenser temperatures. With this type of condenser, the zinc loss in the uncondensed gases, as obtained in actual operation, approaches closely the theoretical amount of zinc vapor indicated by the vapor-pressure curve for any given temperature and pressure condition. When the condensers are operating in the temperature range of 500° to 525°C., blue-powder formation is of the order of 1 per cent of the zinc produced.

A control board is provided for each unit of the condenser. It is equipped with the following control devices: (1) draft gauge, showing the suction in the vapor

pyrometer, indicating the metal temperature in the condenser; (4) vacuum gauge; (5) U-tube gauge for vacuum; (6) valves and piping through which differential pres-

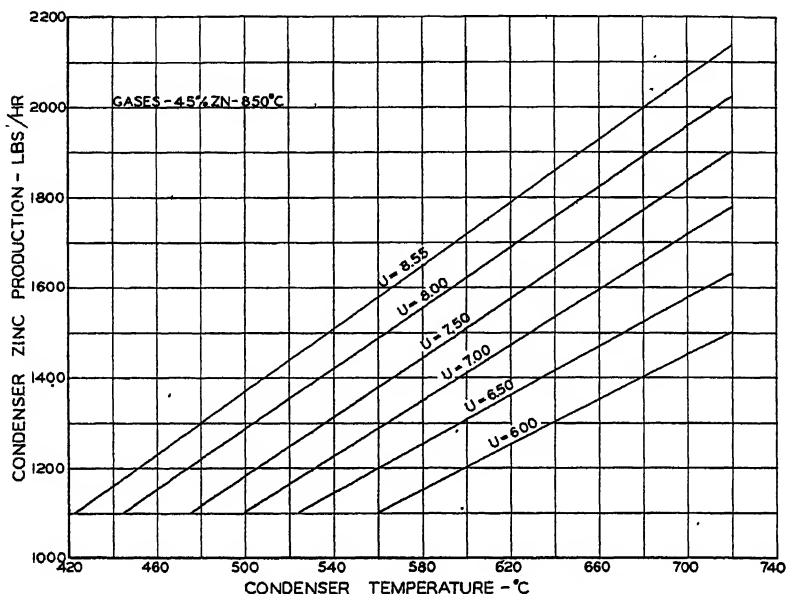


FIG. 7.—RELATION BETWEEN ZINC PRODUCTION AND CONDENSER TEMPERATURE FOR DIFFERENT VALUES OF HEAT-TRANSFER COEFFICIENT, 22-FOOT CONDENSER.

ring (measured in inches of water and kept around 0.5 to 1.5 in. of water); (2) U-tube gauge as a check on the draft gauge; (3)

sure between any two given points in the vacuum system can be checked; (7) push button for control of motor on vacuum control valve.

TABLE 1.—Uncondensed Zinc Vapor, at Equilibrium Conditions

Condenser Temperature, Deg. C.	Vapor Pressure of Zinc, Mm. Hg	Theoretical Minimum Uncondensable Zinc as Percentage of Slab Zinc Produced*
450	0.43	0.2
500	1.30	0.5
550	3.87	1.5
560	4.80	1.8
570	6.00	2.3
580	7.40	2.8
590	9.00	3.5
600	11.00	4.4
610	13.20	5.4
620	16.00	6.5
630	19.00	8.0
640	22.50	9.7
650	26.70	11.9
700	60.00	36.3

* At 16-in. Hg vacuum (29.2 in. Hg barometer) and 45 per cent Zn vapor, 55 per cent noncondensable gas mixture entering condenser.

OPERATING PROCEDURE

Start-up and operating procedure is briefly as follows: After the furnace is filled with the starting charge and power is applied, a temporary gas burner is put into the vapor-ring connecting box to heat the condenser. Hot gases are pulled through the condenser by a fan temporarily attached to the outlet of the washer. A temporary brick dam in the connecting box isolates the condenser from the furnace during the warming up period. Some 10 to 12 hr. after the application of power to the furnace, the furnace temperature is up to normal smelting temperature and the condenser is hot enough (750° to 800°C.) to receive

the initial charge of molten metal (priming). The gas burner is subdued and molten metal is brought, in ladles holding some 1400 lb. of metal, and poured into the tap-

11 tons of molten metal is required to prime the 22-ft. condenser and 17 tons to prime the 31-ft. condenser. Starting vacuum is usually about 6 to 8 in. This is allowed to

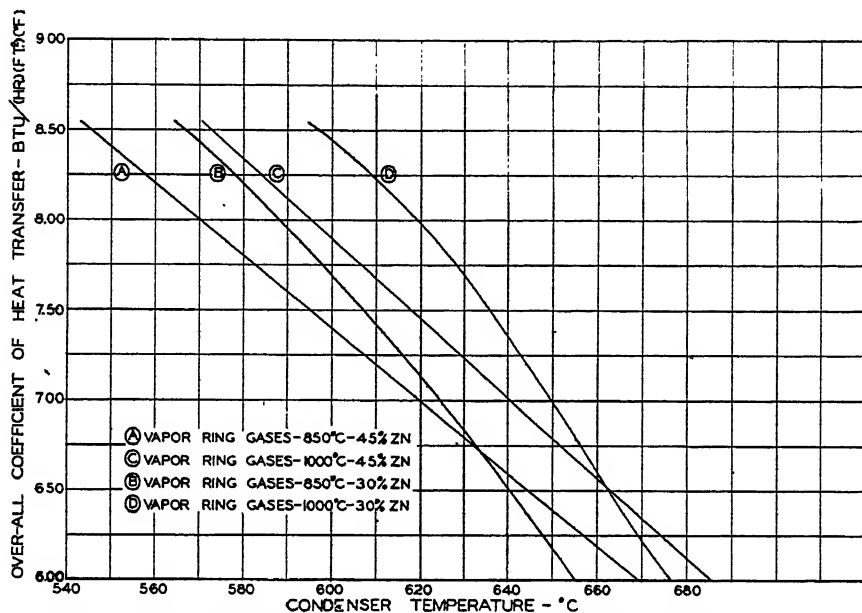


FIG. 8.—RELATION BETWEEN OVER-ALL HEAT-TRANSFER COEFFICIENT AND CONDENSER TEMPERATURE BASED ON:

1. Constant vapor production of 23.4 mols zinc per hour.
2. Wetted area in condenser of 172 square feet.
3. Average suction in upleg of 11.8 Hg.
4. Average temperature of spray water in contact with condenser shell of 65°F.

ping well through a short launder. The tapping well is a simple standpipe alongside the condenser. It is brick-lined and insulated and has a connecting opening to the bottom of the condenser, several feet from the gas-inlet end of the condenser. Metal ladles are handled with an electric crane and hoist.

When several metal furnaces are in operation, priming metal is tapped out of the operating condensers. Provision is made for melting of priming metal in a melting furnace when metal from other furnaces is not available. Priming operation takes 60 to 90 min., after which all vapor-ring and condenser-gas passages are cleaned out, doors are closed and vacuum applied, starting the condenser operation. About

rise to 12 to 14 in. before the first tap is made; thereafter tapping is timed according to vacuum that can be maintained. As the metal level in the condenser rises by accumulation of condensed metal, increasingly higher vacuum is required to maintain the slight negative draft in the furnace. The higher the metal level in the condenser during operation, the higher the heat dissipation and the condenser efficiency. As soon as a ladle of metal is tapped, vacuum in the upleg drops several inches. The condenser is allowed to run until the vacuum rises again to tapping range. The taphole in the tapping well is some 6 in. below the metal level for normal operation. Wetted asbestos is used to close the taphole. A tap-

out hole at the bottom of the tapping well is used to empty the condenser.

MAINTENANCE

Normally, every third day all gas passages in furnace vapor ring, connecting box,

into the condenser but is confined only to the roof portion where the gases come in contact with the brick work. The accumulation is heaviest at the roof of the elbow, where the gas stream enters the metal bath, tapering off within a few feet. These accre-

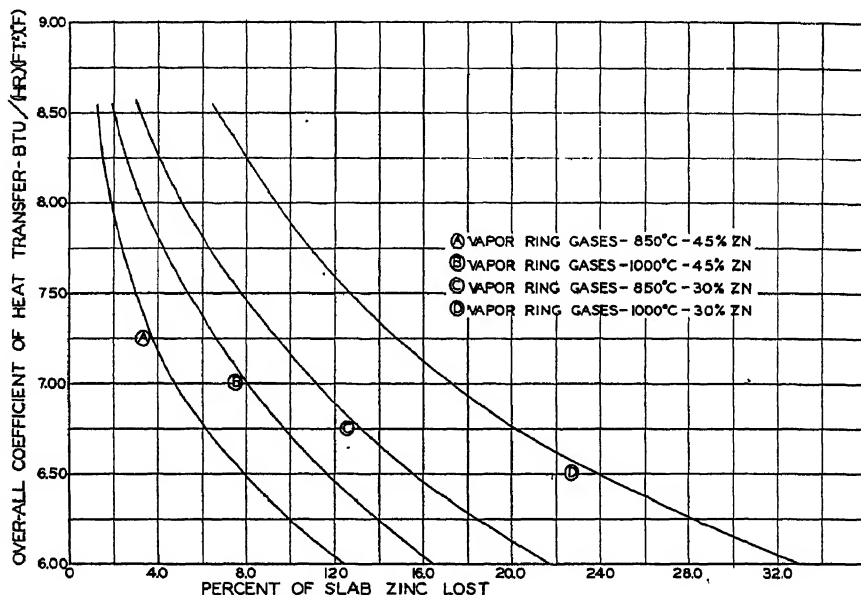


FIG. 9.—RELATION BETWEEN OVER-ALL HEAT-TRANSFER COEFFICIENT AND ZINC LOSS BASED UPON:
 1. Constant vapor production of 23.4 mols zinc per hour.
 2. Wetted area in condenser of 172 square feet.
 3. Average suction in upleg of 11.8 Hg.
 4. Average temperature of spray water in contact with condenser shell of 65°F.

downleg and upleg of the condenser, and the washer are given a general cleanout.

While the rock oxide formation in the vapor ring and the connecting box passages are cut with chisel bars, the accretions in the vertical downleg of the condenser are cleaned with a boring screw, consisting of a double flight 16-in. diameter screw with a double, hard-faced cutting edge, set in a pipe and driven by a vertical motor-speed reducer set. The cleanout screw is suspended from a traveling crane hoist and is lowered into the downleg while the screw rotates and bores the hole. Cuttings are discharged from openings near the top of the enclosing pipe. The rock oxide accumulation in the downleg carries some distance

tions are cut out occasionally through a door provided for this purpose. On rare occasions it becomes necessary to tap out the metal, to chisel out the rock oxide accumulation in the condenser roof, the operation requiring 4 to 6 hr., after which the condenser is primed again and operation resumed.

Occasionally the furnaces have to be shut down prematurely because of failure of the brick lining of the condenser. The main cause of brick failure is occasioned by initial spalling of some individual brick or bricks in a unit, owing to progressive expansion of the refractory and consequent development of excessive pressures. Spalling of brick usually is followed by loosening

of adjacent members. As soon as a brick is dislodged, it floats to the top of the molten metal, and is easily detected by the hammering noise it makes as it is thrown against the lining by the motion of the metal. The condenser is stopped immediately and bricks and debris floating on top of the metal are taken out and examined. If the brick are merely spillings or from the baffles, chances are that the condenser will continue operating. However, close watch is kept and if the iron content of the metal begins to go up it is a sure sign that some part of the steel shell is exposed to molten metal, and the unit is taken out of service immediately. Erosion effect is practically nil.

Maintenance of the condenser proper is confined mainly to refractory lining. Occasional cracks in the steel shell are repaired by welding. Carbofrax lining in the connecting box and downleg, and also the upleg above the metal line and the tapping well, last practically indefinitely. The most vulnerable section of the main condenser lining is the roof region near the gas-outlet end, with an average life of about 5 months; most of the brickwork in corrugated sections of the shell enclosing molten metal averages two campaigns. Life of the lining at uncorrugated portions of the shell is longer, averaging about 12 months. Mica interlining is always renewed wherever repairs are made to the brick lining.

Labor required to tear out the condenser lining from the bottom of the downleg to the bottom of the upleg and to install new

mica and brick lining is approximately 215 man-hours for bricklayers and 275 man-hours for bricklayers' helpers.

To clean out a condenser after a campaign and put it in readiness for a new run, with but few minor repairs, requires some 60 to 75 man-hours of bricklayers and 100 man-hours of helpers.

To rehabilitate a furnace and condenser unit requires 10 to 15 days, depending on the condition of the brickwork. On the average, metal units can be operated with 10 to 12 per cent time lost for rehabilitation.

THE FUTURE

We feel that the development of the vacuum condenser along with the electro-thermic furnace has been a step forward toward the realization of relatively large zinc-smelting units of compact design, with resultant higher efficiency, economy of operation and reduction to minimum of hot and dirty work usually associated with zinc-smelting operations. In this development work, many men in the Josephstown smelter organization, operators, supervisors, technical staff and the officials of the St. Joseph Lead Co. have shown a keen interest and have contributed the ideas that have made possible the solution of many problems encountered; and if the past performance may be taken as a criterion, it is not hard to visualize the trend toward larger capacity and more efficient electro-thermic zinc-smelting units at this plant in the years to come.

Direct Production of Metallic Zinc from Lead Blast-furnace Slag

By W. T. ISBELL,* AND CARLETON C. LONG,† MEMBERS A.I.M.E.

ZINC recovery from lead blast-furnace slags has heretofore been an indirect process, involving, first, the fuming off and collecting of an impure zinc oxide, and second, the reduction of the zinc portion of this oxide to metal either by electrolytic or pyrolytic means. (In a variation of this process, blue powder is the intermediate product rather than zinc oxide fume.)

In 1940, W. T. Isbell proposed that molten slag from the lead blast furnace or stock-pile slag melted down in a blast or stock-pile furnace be charged directly into an airtight container (i.e., furnace) provided with means to heat further the slag by passage of electric current and means to introduce the carbon (coke) necessary to reduce the ZnO constituent of the slag to zinc as a zinc vapor and CO. He also proposed that the zinc vapors so obtained be condensed in a Weaton-Najarian† internal condenser directly connected to the proposed furnace.

It was thought that the Weaton-Najarian condenser could liquefy zinc vapor from lean mixtures of vapor and noncondensable gases. Such condensers have been in commercial use§ since 1936 at Josephtown smelter, where the source of zinc vapor is a column of coke and zinc-bearing sinter electrically heated (charge resistor). Condenser output when

supplied with vapor-gas mixtures containing approximately 45 per cent zinc and 55 per cent noncondensable gases, varies from 18 to 30 tons of slab zinc per day per condenser, depending upon the heat-transfer area (length) of the condenser and the volume of vapor (furnace size) fed to it.

Lead-smelting operations at the St. Joseph Lead Company's plant at Herculanum, Mo., produce a slag containing 12 to 16 per cent zinc. For several years this slag has been stock-piled with the object of recovering the zinc values if and when a commercial method was invented.

Evaluation of the possibilities of the proposed method was made by pilot-plant operation at Josephtown. The first plant, designed in 1940 and operated in early 1941, consisted of a single-phase, two-electrode furnace. The evolved vapors were burned. Electrical characteristics of the molten slag, power requirements, coke requirements, and extent of zinc elimination indicated the feasibility of the proposed method. In the latter part of 1941 a second pilot furnace was constructed, to which was attached a small (6 ft. long) Weaton-Najarian condenser in order to develop an over-all picture of zinc-in-slag to zinc-in-slabs. This furnace was operated in the early part of 1942 and yielded such promising results that a decision was made to design and construct a commercial furnace.

Feed for the pilot-plant furnaces was granulated slag. A suitable deduction (300 to 350 kw-hr. per ton slag) was calculated in estimating power require-

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‡ U. S. Patent 2070101 (Feb. 9, 1937).

§ See page 165, this volume.

ments for the molten slag to be fed to the commercial-size furnace.

Construction of the large furnace at Herculeum was started in the last half of 1942, and preliminary operations were initiated in July 1943.

DESCRIPTION OF PLANT

The electric slag-stripping furnace is in line with and north of the blast furnaces and is served by the same electric tram line that leads to the slag granulators and storage dump. Slag pots from the blast furnace are lifted, by a car-platform elevator, into register with a short launder leading to the slag feed hole in the south end of the electric furnace.

The electric furnace takes the form of a horizontal cylinder of 1-in. plate, 42 ft. 0 in. long inside by 15 ft. 4½ in. outside diameter. The end walls are appropriately stiffened by rib construction. The cylindrical part of the furnace shell and the vapor-offtake boxes are water-cooled by external sprays. Refractory lining of the upper half of the furnace consists of outer arch of 9-in. firebrick within which is sprung a 9-in. arch of forsterite brick. Furnace bottom, laid on 12-in. firebrick, is of fitted carbon blocks and is 3 ft. thick when new. End walls are 29½ in. thick, giving a net inside length of 37 ft. 1 in. and an equivalent inside diameter of about 11 ft. Slag is fed through a small, water-cooled hole in the south end wall of the furnace, about a foot above the maximum slag level. Spent slag is withdrawn through a conventional water-cooled tap block in the north end wall of the furnace. A refractory-lined taphole at lower elevation permits egress of iron and matte. Tapping is into ladle cars for haulage to granulators, or other disposal.

Electric power is introduced by six carbon electrodes of 30-in. diameter, approximately 27 ft. long, disposed linearly along the top of the furnace on 5-ft. 6-in. centers. Power is delivered by

the Union Electric Co. at 33-kv., 60-cycle, three-phase clockwise rotation. Two circuit breakers are provided, one 500,000-kva. interrupting capacity breaker for the furnace power; one 250,000-kva. interrupting capacity breaker for the auxiliary power. The latter is stepped down to 2300 and 440 volts. The furnace power is split into two three-phase circuits, each with its own disconnects. The two three-phase water-cooled furnace transformers are nameplate-rated at 5000 kva. and are equipped with motor-driven tap changers covering the range 100 to 200 volts in five steps. The transformers are preceded by on-load step-voltage regulators, which adjust voltage plus or minus 10 per cent in 0.625 per cent steps, giving an over-all voltage range, bus to bus, of 90 to 220 volts. Secondary buses are connected in delta and interleaved from winding to flexibles. Nominal full load current is 30,000 amp. per phase.

Electrodes are carried by water-cooled copper clamps of the single wedge type and are raised and lowered by motor-driven staffs. Flexibles are designed for 5 ft. maximum of electrode travel. Electrode staff motors at present are manually controlled; provision is made for use of automatic raise-lower control if desirable later on.

Electrode passages into the furnace are sealed by a cylindrical skirt of which the upper end is clamped around the electrode and the lower part is immersed in a water-filled annular chamber surrounding the aperture.

Gaseous reaction products leave the furnace through two openings in the upper part of the east side. Each vapor passageway leads to a 31-ft. long Weaton-Najarian condenser with associated Long-Deeley* gas dedusters. Vacuum is induced by one of two Ingersoll-Rand 36 by 14-in. dual-cylinder type XRE compressors driven

* U. S. Patent No. 2298139 (Oct. 6, 1942).

by axially mounted 225-r.p.m., 250-hp. synchronous motors. Carbon monoxide, discharged by the vacuum pump at near atmospheric pressure, is compressed for delivery to the fuel-gas distribution main by a 14½ by 10-in. dual-cylinder compressor driven by a 150-hp., 360-r.p.m. motor.

Metal tapped from the condensers is transferred to a 90-ton settling furnace, where excess lead settles out and from which the zinc is cast into ingots. Metal is of good Prime Western grade, containing about 1 per cent Pb.

Reduction carbon is supplied by breeze coke thrown on top of the slag bath, throughout its length, by a Deeley coke flinger. Coke is dried by passage through a concurrent gas-fired rotary drier and is apportioned out from dried-coke storage by a constant-weight feeder.

A central control room contains instruments pertaining to furnace and condenser operation. The electric power panel provides the following indications and functions:

For total power load: demand meter, kilowatt-hour meter.

For furnace power: megawatt meter, kilovolt meter with transfer switch, ammeter with transfer switch.

Kilowatt-hour meter.

For each of the two three-phase electrode circuits: voltmeter (bus to ground) in each phase, mega-ammeter in each phase, megawatt meter, megavarmeter, kilowatt-hour meter, on-load voltage regulator control with Selsyn driven position indicator, transformer tap-changer control and signal lights, electrode staff raise-lower controls.

For auxiliary power: standard unitized metal-clad switch gear.

Control switches for oil circuit breaker.

The condenser control panel features vapor offtake indicating and recording pressure gauges, condenser exit vacuum gauge, gas-deduster differential pressure gauge, vacuum supply-line gauge, vacuum control-valve position indicator (Selsyn

driven) vacuum-control-valve motor push buttons and signal lights, condenser-spray water-pressure gauge. This equipment is in duplicate, one for each condenser. The same panel also contains a null-type potentiometer temperature indicator with suitable transfer switches to accommodate Chromel-Alumel thermocouples in the vapor offtakes, the condensers, the zinc-casting furnace, and so forth.

OPERATION

The operation, briefly outlined, comprises the following steps:

1. Molten slag is teemed from pots into the electric furnace.
2. Coke is distributed over the pool of slag in the furnace.
3. Heat is developed by passage of electric current through the pool of slag. Slag-bath depth varies from 10 to 30 inches.
4. Zinc vapor and carbon monoxide pass to the condenser, from which the condensed zinc metal is tapped into ladles and transferred to the holding furnace.
5. Stripped slag is tapped into pots and sent to slag granulators.

The operation proceeds essentially on a continuous basis, though the slag feed and discharge are semicontinuous.

Molten slag is delivered from the blast furnaces in ladle cars. These were formerly of about two tons net capacity but at present are being replaced by ladles of nominal 4.4-tons gross capacity (approximately 2.9 tons net capacity). The molten slag weighs about 250 lb. per cu. ft. Elevation of the slag-ladle car is followed by tapping into the electric furnace through a cast-iron launder and water-cooled feed hole. This hole is plugged when slag is not being run.

Power input is regulated in accordance with the amount of slag being fed, about 600 to 650 kilowatt-hours per ton of slag being required for a 12 per cent zinc slag and somewhat more power for richer slags.

As a general practice, the lower voltage taps are employed. The individual electrode positions are adjusted so that, approximately, the current and voltage to ground readings are the same for all six "legs," as the electrode circuits are colloquially called.

Condenser vacuum is adjusted by a valve operated by push button, so that the furnace is under slight positive pressure (about one inch of water). A characteristic of Weaton-Najarian condensers is the "breathing" action induced by the to-and-fro movement of the molten metal. Thus, while the average pressure inside the furnace may be 1 to 2 in. of water, instantaneous pressures of plus or minus 5 in. of water are frequently observed.

As zinc is condensed and accumulates in the condenser, more vacuum is required to "pull" the gas through the condenser. Thus the vacuum-gauge reading (at a given gas-flow rate) is an indication of the amount of metal in the condenser and serves as a guide to time to tap the condenser. Condensers usually are tapped when the vacuum reaches 14 to 15 in. Hg, the vacuum falling about an inch more or less with the removal of 1500 lb. of metal.

Slag tapping keeps pace with slag feeding. Slag depth is measured by a bar let down through a hole in the furnace roof. Slag fall is approximately 80 per cent of the weight of incoming slag when the latter contains 12 to 13 per cent Zn. Optical-pyrometer measurements indicate the exit slag to have a temperature of 1350° to 1400°C. Preliminary observations indicate that, within limits, this temperature is a function of reactions occurring inside the furnace, as increase of power does not increase temperature markedly but instead causes increased evolution of zinc until zinc elimination is substantially complete.

Matte and iron tend to settle toward the bottom of the furnace and are tapped periodically through a 3¼-in. refractory-

lined taphole. It is intended to return the matte and iron to the lead plant after suitable granulating means have been provided.

Not all of the incoming sulphur follows the exit matte. Part of the sulphur is evolved as lead sulphide vapor, passes through the condenser, is precipitated in the gas-dedusting apparatus and finds its way to what, in the vernacular, are called the "blue-powder ponds." Through these, a series of four settling ponds, the gas washer water flows. Settled matter consists principally of zinc metal (partly oxidized by the water), lead sulphide and general junk or "fly-ash," probably representing slag-spray droplets resulting from turbulence in the furnace. When the accumulation is large enough to make it worth while, it is planned to recycle the material in the blue-powder ponds through the lead plant to recover the lead and to enrich the slag with zinc.

Interdependent relationships exist among amount of coke fed, power input, degree of zinc elimination, electrode consumption, and amount of iron reduced. In general, as coke consumption is increased, the power input, zinc elimination, and iron reduction all increase while the electrode consumption decreases. These relationships were disclosed by the pilot-plant tests. With the furnace of commercial size, operations have for the present been confined to coke consumptions approximately equivalent to the amount of zinc in incoming slag. Under these conditions the amount of reduction of iron that occurs is small, as the slag analyses reveal.

The stripped slag sample reported on was obtained by spoon from the top of the ladle. This method of sampling, while convenient for routine control work, appears to yield low values for zinc, inasmuch as a composite sample of stripped slag shipped from the granulator pits contained, for the same period, approximately 4.0 per cent Zn.

TABLE 1.—*Slag Analyses*

Slag	Analysis, Per Cent									
	Pb	Cu	SiO ₂	FeO	CaO	MgO	S	Zn	Al ₂ O ₃	Ag
Blast-furnace.....	2.65	0.56	26.0	35.4	8.1	4.1	2.6	12.9	3.8	tr.
Stripped.....	0.10	0.11	32.3	35.3	10.8	6.5	1.5	2.8	9.0	

Material derived from the matte-iron taphole varies widely in composition, depending on how much slag is entrained. A typical analysis of matte-iron composite containing little or no slag is: Pb, 1.6 per cent; Cu, 7.8; insoluble, 0.2; Fe, 58.1; S, 27.4; Zn, trace; Ni-Co, 1.9.

At the present writing the wedge-shaped carbon block lining, described above, is being installed. The original furnace bottom was built of rammed carbon paste, reinforced with old carbon electrodes. This carbon paste material exhibited an unexpected degree of reactivity, with the result that it became consumed and permitted the reinforcing carbons to rise and float. Actual operating experience to date is therefore meager. During the last campaign slag was fed at the rate of approximately 100 tons per day. Apparent zinc elimination (ratio of weight of zinc in the incoming slag to the weight of zinc remaining in the outgoing slag) was about 75 per cent. Single-pass recovery (ratio of weight of slab zinc produced to weight of zinc in entering slag) was approximately 55 per cent of the entering zinc. The remaining 20 per cent of zinc represents losses to the atmosphere and material transferred to the blue-powder ponds.

Slag-handling equipment is now being modified to permit faster feed rates. From the observations of the preliminary oper-

ations, it appears that the furnace can process 250 to 300 tons of slag a day unless a limitation is encountered in the practical reaction rate per unit hearth area.

Operating force per shift consists of a shift foreman, furnace operator and helper, two tappers and two tappers' helpers, a control-room operator, a "slag motorman" (to haul stripped slag to granulators), and a general helper (two on day shift). This does not include the metal-casting labor, as this work is handled by the lead-refinery crew.

While a good deal of development work remains to be carried out, particularly in regard to mechanical contrivance, the preliminary operating results have been even more encouraging than were hoped for. The design specifications laid down for commercial operation envisioned a power consumption of 800 kw-hr. per ton of (14 per cent Zn) slag, coke consumption not over 7.5 per cent of slag weight, gross electrode consumption not over 10.5 lb. per ton of slag, stripped slag to contain not over 20 per cent of the charged zinc, single-pass recovery (as slab zinc) to be 68 per cent, over-all recovery (as slab zinc) to be 75 per cent of the zinc in the slag feed. In the light of the preliminary operating experience there appears little doubt but that these specifications will be met with margin to spare.

World Survey of Electrolytic Zinc, 1936-1943

By ARTHUR A. CENTER,* MEMBER A.I.M.E.

WORLD production of electrolytic zinc has shown an increase for each year since 1932. Production up to 1936 was summarized in my earlier paper [*Trans.*

ceased. While the period reflects preparations for and the carrying on of the present war, electrolytic zinc proved its value in many industries as a peacetime metal in the years from 1919 to 1940.

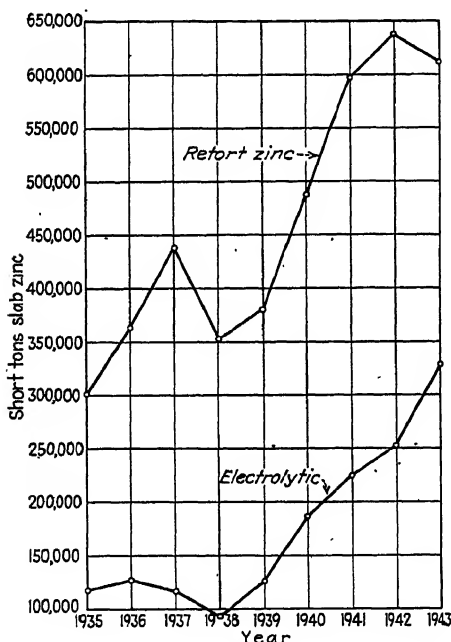


FIG. 1.—PRODUCTION OF ELECTROLYTIC AND RETORT ZINC IN THE UNITED STATES.

A.I.M.E. (1936) 121, 453-464], and this present paper carries the subject through 1943.

During this time of increase, it is safe to say that the average purity has been raised more or less continuously, and the amount of four-nines metal has been in-

TABLE 1.—World Survey of Production of Electrolytic Zinc, 1936-1943*
TONS

Year	Total U. S. Primary Zinc	Electrolytic Zinc			Retort Zinc, U. S. Primary
		World ^b	U. S.	Foreign ^b	
1935	420,634	552,000	118,476	433,794	302,158
1936	492,132	594,000	127,175	466,825	364,957
1937	556,904	609,000	117,511	491,489	439,393
1938	446,341	620,000	93,272	526,728	353,060
1939	507,236	662,000	127,056	535,000	380,180
1940	675,275	720,000	187,041	532,960	488,235
1941	822,020	798,000	224,313	573,687	597,707
1942	891,872	832,000	252,987	579,013	638,885
1943	942,309	858,000	329,902	528,098	612,407

* The figures in the tables are variously from the United States Bureau of Mines, the American Bureau of Metal Statistics, or have been supplied by the writer.

^b Estimate.

World production (Table 1) increased from about 594,000 tons in 1936 to around 858,000 tons in 1943; United States production increased from 127,171 tons to 329,903 tons for the same years. Total production of primary zinc in the United States is given in the first column of Table 1; retort production of primary zinc, obtained by difference, in the last column. The curves drawn from these figures are shown in Fig. 1. They represent continuations of the curves in the earlier paper that cover commercial production of electrolytic zinc from its inception in 1915 to 1935.

The earlier paper gave data for total world production and foreign retort production (calculated therefrom) and showed curves of electrolytic vs. retort production

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of zinc outside of the United States. These data and curves are too much of a guess for the years 1939 to date, and so are omitted in the present article. However,

Flash, or suspension roasting as developed at Trail was described in 1936 (*Trans.*, Vol. 121). Since the Trail installation, furnaces of this type have been built

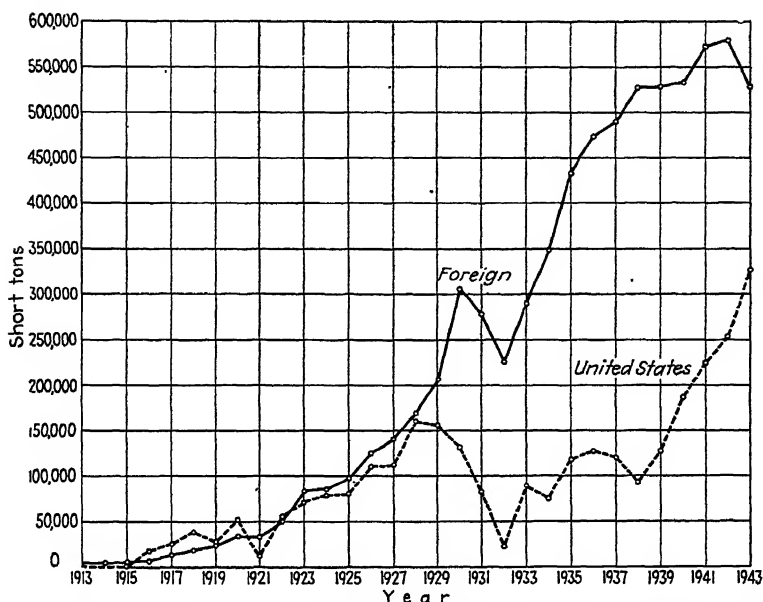


FIG. 2.—PRODUCTION OF ELECTROLYTIC ZINC IN THE UNITED STATES AND FOREIGN COUNTRIES FROM 1915 TO 1943.

one could hazard the guess that foreign retort production of primary zinc fell and production of electrolytic zinc rose until they reached about the same amount in 1941.

Production of electrolytic zinc by countries is given in Table 2 for the years 1936 to 1938, and for the United States and Canada to 1943. Productions in the rest of the world are given by continents beginning with 1939, but these represent only more or less intelligent guesses based on participation in the industry since its start. Fig. 2 shows the curves for United States and foreign production of electrolytic zinc from 1915 to 1943. It is to be noted that the United States did not equal its 1929 production rate until 1940, while foreign production never fell back to its 1929 rate and climbed uninterruptedly from 1932 until 1942.

for several plants, among them the Giesche Spolka Akcyjna in Poland, the Monsanto plant (East St. Louis), and the Corpus Christi plant (American Smelting and Refining Co.).

Where higher grade zinc concentrates (less, iron, silica, lead, etc.) can be obtained, there has been a tendency to simplify leaching-plant operations by using a single instead of a double leach; also mechanical agitation in leach tanks, to simplify and to keep down temperature losses. To help toward making purer metals, zinc-dust purification practice tends toward precipitating copper and cadmium in different stages with intermediate filtering.

Construction of electrolyzing cells still is not uniform. Trail found rubber-lined tanks more satisfactory than its original lead-lined concrete tanks, but Hudson Bay

found a rubber lining unsatisfactory. Trail found Prodorite tanks still better and the Anaconda company has built several units using Prodorite, but the Monsanto plant

num-reduction plants have installed several score of these machines in the past 10 years.

The use of silver-lead anodes, as de-

TABLE 2.—*Production of Electrolytic Zinc by Countries**
TONS

Country or Continent	Capacity Cathode Zinc per day	1936	1937	1938	1939	1940	1941 ^a	1942 ^a	1943 ^a
United States:									
A.C.M. Co., Great Falls, Mont.....	440	89,360	71,329	70,763	101,000	107,268	118,888	130,272	158,825
Anaconda.....	213	16,588	23,351	6,875	7,629	42,296	57,518	63,214	78,761
Sullivan Mining Co.....	105	21,223	22,831	15,634	18,427	37,477	39,285	39,916	41,129
American Zinc Co.....	98						8,622	15,988	25,061
American Smelting and Refining Co.....	70							3,597	26,127
Canada:		127,171	117,511	93,272	127,056	187,041	224,313	252,987	329,903
Consolidated Min. and Smelt Co.....	450	119,478	124,157	133,242	136,810 ^a	147,000 ^a	165,134	165,249	152,299
Hudson Bay Min. and Smelt Co.....	150	32,219	34,486	38,414	38,790	45,000 ^a	48,510	50,622	54,249
North America.....		151,697	158,643	171,656	175,600	192,000	213,644	215,871	206,548
Norway: Norske Zinkkompani.....	150	278,868	276,154	264,928	302,656	379,041	437,957	468,858	536,451
U.S.S.R.: Ordzhonikidze... Cheliabinsk.....	75 } 75 }	49,361 40,000 ^a	45,492 45,000 ^a	51,257 45,000 ^a					
Germany: G. von Giesche's Erben.....	200	42,237	44,501	60,000 ^a					
Poland: Giesche Spółka Akcyjna.....	66								
Slaskie Kopalnie Cynkownie.....	22 }	20,630	21,571	20,806					
France: Vieille Montagne... Belgium: Vieille Montagne	110 } 30 }	22,485 7,017	27,158 8,668	31,729 9,016					
Italy: C. I. E. Liguri... Soc. Monteponi (Sardinia).....	10 } 20 }								
Soc. Min Met Pertusola Soc. Montecatini-Montecatchio.....	36 } 60 }	21,000	33,000	30,392					
Europe.....		202,730 ^a	225,390 ^a	248,200 ^a	245,000 ^a	212,000 ^a	225,000 ^a	226,000 ^a	196,000 ^a
Rhodesia: Rhodesian Broken Hill Dev. Co....	70	23,218	15,714	11,440					
Japan: Nippon Soda, Fukushima-Ken.....	20	2,800							
Mitsubishi, Hosokura... Mitsubishi, Naoshima..	27 } 20 }	3,084 4,952	13,500	17,000 ^a					
Africa and Asia.....		34,054	29,214 ^a	28,440 ^a	34,000 ^a	36,000 ^a	42,000 ^a	44,000 ^a	44,000 ^a
Australia: Electrolytic Zinc Co. of Australasia.....	225	77,788	78,102	78,198	79,766	93,000 ^a	93,000 ^a	93,000 ^a	82,000 ^a
Total.....		594,000 ^a	609,000 ^a	620,000 ^a	662,000 ^a	720,000 ^a	798,000 ^a	832,000 ^a	858,000 ^a

* See footnote a under Table 1.

^a Estimate.

did not get good results with Prodorite. Prodorite is an asphaltic product said to have a base on the order of gilsonite. Its use for cells was first pushed by Trail.

Choice of electric power conversion equipment in zinc plants, is definitely toward mercury-arc rectifiers. The alumi-

veloped at the Sullivan plant, to produce 99.99+ per cent zinc spread during the period under review. The controlled use of cobalt in the electrolyzing solution has been found to help reduce the lead content of zinc cathodes, as also has electrodeposition of a layer of lead on cast lead anodes.

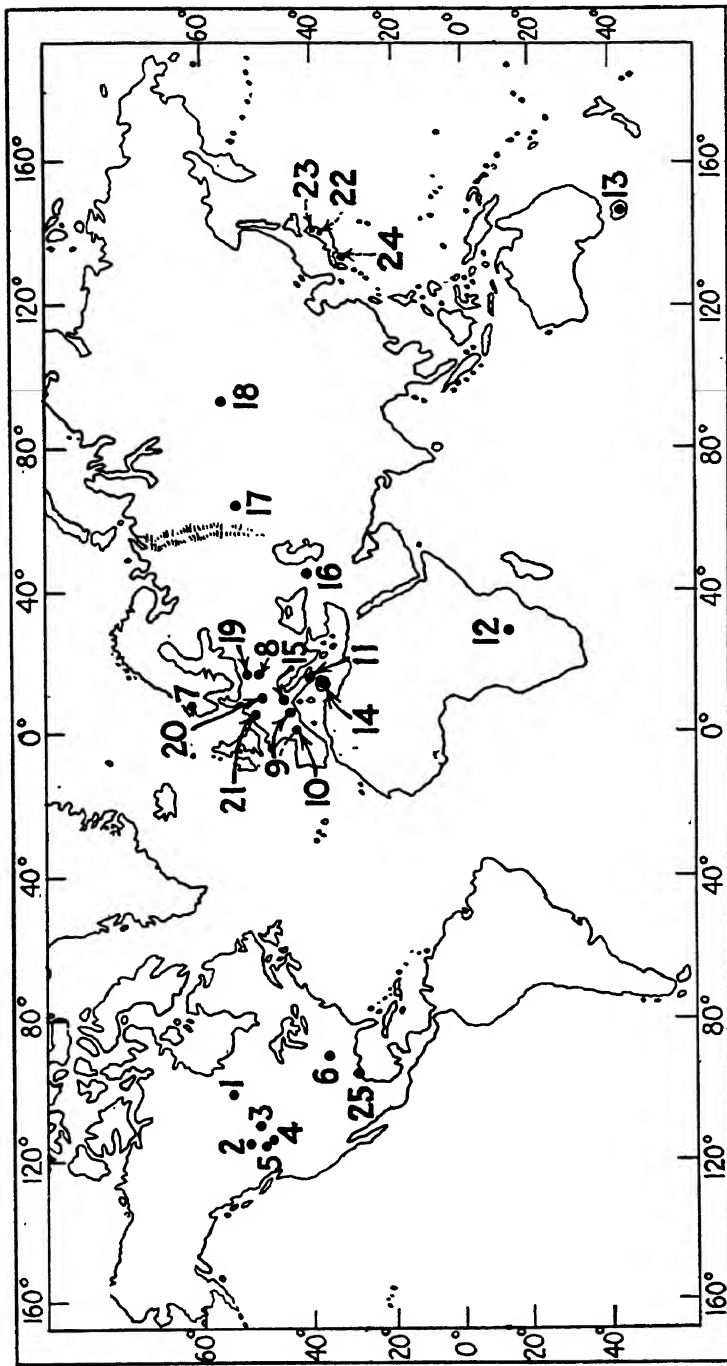


FIG. 3.—LOCATIONS OF ELECTROLYTIC ZINC PLANTS.

- | | | |
|-------------------------------|-----------------------------------|-----------------------------------|
| 1. Flin Flon (Hudson Bay). | 13. Electrolytic Zinc Co. of Aus- | 19. Slaskie Kopalne i Cynkownie. |
| 2. Consolidated. | 14. Monteponi. | 20. von Giesche's Erben (German). |
| 3. Anaconda Copper Mining Co. | 15. Montecatini-Montevecchio. | 21. Vieille Montagne (Belgium). |
| (Great Falls). | 16. Ordzhonikidze. | 22. Nippon Soda. |
| 4. A.C.M. (Anaconda). | 17. Cheliabinsk. | 23. Hosokura. |
| 5. Sullivan. | 18. Kemerovo. | 24. Naoshima. |
| 6. American Zinc Co. | | 25. American Smelt. and Ref. Co. |

Fig. 3 shows the locations of the electrolytic-zinc plants in different parts of the world.

Developments in the various countries from 1915 to 1936 were given in my articles in *Mining and Metallurgy* (November 1929) and in Volume 121 (*op. cit.*). A brief statement of developments from 1936 to date follows.

UNITED STATES

The Sullivan plant was enlarged by 50 per cent in 1937, giving it a capacity of 105 tons of cathode zinc per day. A description of the plant before enlargement was given in 1936 in Volume 121 of the *TRANSACTIONS*. The roasting department consisted of five 25-ft., 7-hearth Wedge furnaces. Two similar furnaces have been added. In the leaching plant, three Burt filters were added to the six previously installed; also additional tanks and filter presses. In the electrolyzing department, 152 cells were added to the original 300, and a third motor-generator set was added. All these additions were alike in type with some small changes in construction.

The Anaconda Copper Mining Co. increased capacity of its plants by 14,000 tons of zinc in 1941. In 1942 it increased its production capacity by 45,000 tons zinc per year, by increasing the number of electrodes in a cell and increasing the current density. The original plant at Great Falls was built for 100 tons cathode zinc per day; the two plants have a present capacity of more than 650 tons cathode zinc per day.

The Evans-Wallower plant was replaced in 1941 by the Monsanto plant of the American Zinc Co., with considerable change in flowsheet and equipment (see page 189, this volume). The plant was doubled in size in 1943. The Corpus Christi plant of the American Smelting and Refining Co. was built in 1942, and is described on pp. 194 to 209, this volume.

All the plants in the United States except Monsanto produce electrolytic cad-

mium from the electrolytic-zinc plant purification residues. Monsanto turns over a cadmium product to the company's general cadmium-distillation plant, in its zinc-retort plant near by. The Anaconda company and the American Smelting and Refining Co. also produce indium from their purification residues.

CANADA

Consolidated Mining and Smelting Co. increased capacity by 50 tons cathode zinc per day in 1941. This company pioneered the use of mercury-arc rectifiers for power conversion. The earlier plant is described in Volume 121 of the *A.I.M.E. TRANSACTIONS*.

The Hudson Bay Mining and Smelting Co. added a fourth electrolytic unit in 1936, also a cadmium plant. In 1940 it added a fifth unit, together with two more Wedge split-draft roasters, leaching and purification equipment and the seventh motor-generator set. The initial plant capacity was more than doubled by these additions. The company's hydroelectric plant at Island Falls was enlarged to keep pace with the greater demands on it. A pilot plant to treat the calcine leach residue by a chlorination process has been in operation. A large stock pile of probably more than 300,000 tons of this material has accumulated since the zinc plant started operations in 1930.

PERU

Cerro de Pasco has been operating a pilot plant of 5 tons cathode-zinc capacity per day and has built its hydroelectric plant.

NORWAY

The Norwegian zinc plant at Eitrheim, not far from Bergen, ran largely in peacetime on calcines from Belgium. The concentrate came from the Reocin (Spain) mines of the Asturienne Company. It was

roasted in Belgium to produce sulphuric acid and the calcine was sent to the cheap hydroelectric power source in Norway. The plant came under German control with the invasion of 1940, of course, and it may be presumed that production has fallen off considerably since that time. A description of modified gas producers at this plant to treat leach residues was given in *TRANSACTIONS*, volume 121.

U. S. S. R.

Each of the plants in Russia has cell-room capacity of 75 short tons cathode zinc per day. However, the estimates given in Table 2 for 1936 and 1937 are probably high rather than low. According to reports, the Cheliabinsk plant was not keeping up its expected 20,000-metric-ton slab zinc per annum. Much of the zinc in the Ural zinc-copper ores has been activated in the mines, making it difficult to obtain a concentrate high in zinc and low in copper. Whether the difficulty is caused by the high copper content and harmful elements associated with the copper minerals or to failure to keep up the required standards of maintenance and cleanliness, is not stated. The Ordzhonikidze plant has operated in the late 1930's with cobalt over 100 mg. per liter. The acid was dropped from 110 to 80 grams per liter at such times and thus the power cost was increased 10 per cent. Cooling water at 7°C. was available. A cell-room unit in either plant consists of 150 cells arranged side by side on one level, and with individual feed and discharge. The current available is 9000 amp. supplied by mercury-arc rectifiers. The current density is about 40 amp. per square foot. The government is naturally keeping secret later developments. The German push into the Ukraine came perilously close in 1942 to the Ordzhonikidze plant and its power sources. How much operations were affected has not been made public.

POLAND

Giesche Spolka Akcyjna changed its two Wedge furnaces to suspension roasting in 1936, but found they had to grind finer to get good results. A comparison of the analyses of the Trail and this concentrate indicates a reason:

Trail: 51 per cent Zn, 11.5 per cent Fe, 32 per cent S
Giesche: 60 per cent Zn, 3 per cent Fe, 31 per cent S

The gas is taken off at the top of the furnaces, which is a point of difference from the Trail installation, and there is no heat recovery as there is at Trail.

The plant, I understand, was not destroyed before the invasion in 1940. With ore sources near at hand, it has probably been operated since then at a substantial rate of its capacity under German control.

FRANCE

Vieille Montagne increased production from its plant at Viviez until the invasion in 1940, the rate being about double at that time compared with the production in 1929. Presumably it too was operated at a fairly high rate of its capacity under German control.

BELGIUM

Belgium has been having trouble holding its markets with horizontal-retort spelter. Its electrolytic zinc plant at Baelen, treating a fume from lead blast-furnace slag, was operating at capacity until 1940.

GERMANY

The Magdeburg plant was enlarged 50 per cent in 1937. The cell room should be good for 200 tons cathode zinc per day. The cell-room basement is on piles below water level and this water carries chlorine. The floor and walls are supposed to form a waterproof chamber. It will be interesting to see whether seepage can be easily kept out as the plant grows older.

A description of the plant before enlargement is given in *A.I.M.E.* volume 121.

The normal source of concentrate is from the company property that is on the German side of the Polish boundary near Beuthen.

Germany has not been able to continue imports of overseas zinc concentrate of any extent for itself or the invaded countries that have electrolytic zinc plants. Much of this material came to the United States plants.

ITALY

Italian production was cut down in 1938 by a serious drought, which caused rationing of the national hydroelectric power supply for some months in the first part of the year. Some of the ores run relatively high in gallium (0.023 per cent), germanium (0.012 per cent), indium (0.010 per cent), and cobalt (0.005 per cent), and efforts are being made to produce these as by-products.

The Italian electrolytic zinc plants on the island of Sardinia and the one at Cotrone on the mainland were captured by the United Nations during 1943. These accounted for half of the Italian zinc production. The latest plant built, at Porto Marghera near Venice, was doubled to 60 tons cathode zinc per day in 1940.

RHODESIA

Rhodesian Broken Hill, drilling below its surface deposits of oxidized ore in 1937, had the good fortune to run into exceptionally high-grade sulphide ore, and has developed about 1,500,000 short tons averaging 35.5 per cent zinc and 23.5 per cent lead. It still has something near 2,000,000 tons of oxide ore left. It has been roasting pyrite to make acid for treating

the oxidized ore and it should now be able to make the acid from the sulphide ore. This necessitated provision in the zinc plant for a high-zinc, low-silica calcine in a plant that has been treating a low-zinc, comparatively high-silica ore. The company was reported as endeavoring to go ahead with additions to the hydroelectric plant in 1940.

AUSTRALIA

The Australian plant has operated at capacity during the period. It built up a supply (over 200,000 tons) of concentrate and calcine at the zinc plant, which is sufficient for two years operation with the aid of its Tasmanian mines. The latter normally supply about one third of requirements. Demand for the metal has exceeded capacity and war demands have caused temporary withdrawal from some markets in India and, of course, Japan. War deliveries to England were contracted for 1940 at the rate of 3000 long tons per month with half-yearly adjustments in prices. A description of the plant is given in A.I.M.E. volume 121.

JAPAN

The Mitsubishi plant in the Miyagi prefecture was enlarged in 1939 to 9000 metric tons cathode zinc per year. An electrolytic zinc plant is reported scheduled for construction in Chosen (Korea), also one in the Okayama prefecture, each of 6000 metric tons per year capacity.

ACKNOWLEDGMENTS

I wish to express appreciation for the various sources of information and publications drawn upon in preparing this paper.

New Electrolytic Zinc Plant of the American Zinc Company of Illinois

By L. P. DAVIDSON,* MEMBER A.I.M.E.

(New York Meeting, February 1942)

THE new electrolytic zinc plant of the American Zinc Company of Illinois commenced operation in April 1941. The simple flowsheet using the standard current density and the economic reasons that dictated it are given herewith.

The Evans-Wallower Zinc Co. built an electrolytic zinc plant at Monsanto, Ill., in 1929 and operated it for about two years. The plant stood idle from 1932 and was purchased by the American Zinc Co. in 1940. Because of the condition of the equipment, excepting the motor generator set, a complete rebuilding was necessary.

The Fairmont City plant of the American Zinc Co. could treat the leach residues, the purification cake and the skimmings from the melting furnace in its various plants. This possibility permitted a simple flowsheet with good economic results.

The flowsheet is shown in Fig. 1. The calcined concentrates are leached in mechanically agitated tanks with spent electrolyte and such ferric iron solution as necessary. When the acid has been neutralized and the iron coagulated, the fluid is discharged to settling tanks. The underflow from these thickeners is filtered on a Moore filter; the filter cake leaves the plant for retreatment and the filtrate joins the thickener overflow.

Zinc dust is added to this solution until the copper and cadmium are precipitated. The pulp is filtered through Shriver presses, which deliver the purified solution to stor-

age tanks, and the copper-cadmium-zinc cake is shipped for retreatment and recovery of these three metals.

The purified solution is electrolyzed; the regenerated acid is returned for use in the leaching plant and the cathode zinc, after stripping, goes to the melting furnace, from which it is cast in slabs. The skimmings from the melting furnace are shipped to the Fairmont City plant for reduction to metal in the retort furnaces.

The choice of this simple flowsheet was made possible only because of the facilities of the Fairmont City plant. The long leaching period, with high acid content and high temperature which characterize the high-density process, gives a higher zinc extraction but also dissolves more impurities, which must be removed. The same is true to a lesser degree of the multi-step leaching of the western low-density plants. By the sacrifice of some initial extraction, solutions can be obtained that are relatively easy to purify and give good ampere efficiency. This loss in initial extraction is made up in the retreatment of the residues in the Waelz plant. The impurities that accompany the zinc thus extracted are inconsequential when the Waelz product is treated in a distillation plant.

It was recognized that this flowsheet would require a somewhat greater amount of sulphuric acid—either as acid or as sulphate sulphur in the calcine—because of poorer washing. The sulphuric acid plant at Fairmont City could deliver 60° Bé. acid to compensate for the sulphate loss and the cost would be less than the cost of more intensive washing.

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The retreatment of the purification cake for copper and cadmium recovery was facilitated by the existence of the cadmium plant. The distillation of the skimmings results in a greater production of net slabs for a given electrolyzing capacity, provided that this material is treated by itself. This possibility exists at Fairmont City and also permits of a very simple handling of the skimmings at the electrolytic plant.

To make consistently Special High Grade Zinc, the electrolyzing cells were equipped with anodes of the lead-silver alloy developed by U. C. Tainton, and ample cooling facilities were provided. In this way the lead content of the zinc produced has been satisfactory.

It is believed that the choice of this flowsheet offered the following advantages over the retention of the high-density flowsheet formerly used in the plant:

1. Cheaper and faster separation of the leach residue from the neutral zinc sulphate solution.
2. Less equipment for the production of the same amount of zinc.
3. Cheaper zinc-dust purification.
4. No necessity for process steam.
5. Greater flexibility in treating various calcines.
6. Lower maintenance costs.
7. Less cooling water.
8. Less labor.

EQUIPMENT

The flowsheet (Fig. 1) and the layout of the equipment (Fig. 2) show the flow of the material through the plant.

The equipment is standard and only the less usual features will be described.

The incoming calcine is unloaded pneumatically and delivered to storage bins. From the bins it is drawn into a feeding car of 5000-lb. capacity, which, after weighing, is spotted at the desired leaching tank. A screw conveyor will empty this car in less than five minutes.

Coarse residue is removed from the neutral pulp by an Allen cone in closed circuit with a Dorr classifier.

All piping is either lead or copper up to the Shriver presses. The lines for purified solution are either rubber hose or steel pipe.

No process steam is used, the heat of reaction being sufficient for adequate solution of zinc oxide and temperature of purification. The temperature in the leaching tanks, at the time of discharge, is about 75°C., with a temperature of 45° to 50°C. in the purification tanks during the addition of zinc dust.

The cell room has 180 lead-lined reinforced-concrete cells arranged in 15 cascades of 12 cells each. The cells are 8 ft. by 4 ft. 10 in. by 2 ft. 10 in. inside dimensions. They are arranged in cascades, six cells in a row, the difference in height being 4 in. Each of the upper five cells has two lead cooling coils set in either end. The bottom cell has one coil only set in the upper end.

The water piping is so arranged that one valve controls the water to four coils. The discharged water flows through a rubber hose onto the basement floor and into the sewer. This protects the concrete floor from acid spills and permits good temperature control. The inlet temperature is about 17°C., and with 1500 gal. per min. for the entire cell room, gives an average cell temperature of 38° to 40°C.

Electrical Substation

Primary power is delivered at 13,200 volts from the Cahokia plant of the Union Electric Co. A part is transformed to 440 volts for auxiliary power, the rest being used at the line voltage by the 8400-hp. synchronous motor for the generation of the electrolyzing current. Two generators of 5000 amp. at 600 volts are operated from the synchronous motor, and, running in parallel, deliver 10,000 amp. of current to the cell room.

The limiting voltage of the generators made it necessary to use very large bus bars for the cells. The average cross section of these bars is 33 sq. in. While at first

rates is as follows: Zn, 51.46 per cent; Fe, 4.12; Pb, 3.23; CaO, 0.52; MgO, 0.26; Al_2O_3 , 0.86; Cu, 1.25; Cd, 0.22; Sb, 0.024; Ba, 2.53; SiO_2 , 0.99.

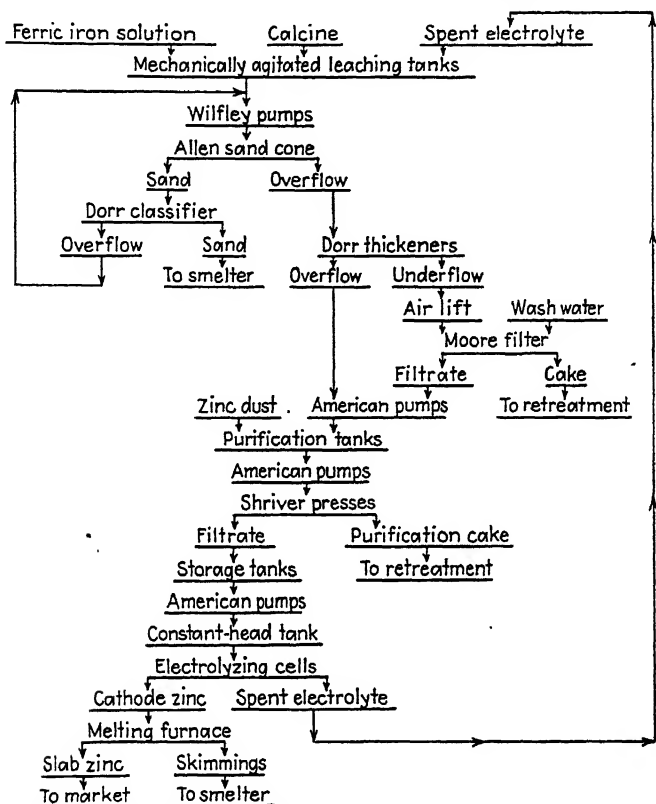


FIG. 1.—FLOWSHEET, ELECTROLYTIC ZINC PLANT, AMERICAN ZINC COMPANY OF ILLINOIS.

glance this appears to be excessively large, the economic and operating results have amply justified it.

METALLURGY

The plant was designed to treat, during the first two years of operation, a large tonnage of concentrates from the Buchans mine in Newfoundland. These concentrates are to be roasted in a flash roaster at the titanium oxide plant of the National Lead Co. at St. Louis, where the sulphur will be utilized for the manufacture of sulphuric acid. An average analysis of these concen-

Because of the late starting of this plant, the feed that has been available for the electrolytic plant has not been primarily from the Buchans concentrates, and to date has not been flash-roasted. In general, the operating procedure has been as planned, but wide variations in the zinc content of the calcines treated have made it difficult to attain the expected metallurgical results.

The leaching is done in batches. About 30 volume tons of spent electrolyte is neutralized with calcine. The acid content of the spent electrolyte is about 13.5 per cent and enough ferric iron solution is added to give 0.5 grams per liter Fe in the

head acid. The actual time of leaching is about 2 hr., and filling and discharging of the tanks takes an additional hour.

The zinc-dust purification has been made

per liter; Co, 0.5 to 1.8 mg. per liter and Ge, 0.4 to 1.8 mg. pre liter. There is little MgO and it has shown no sign of building up in the circuit.

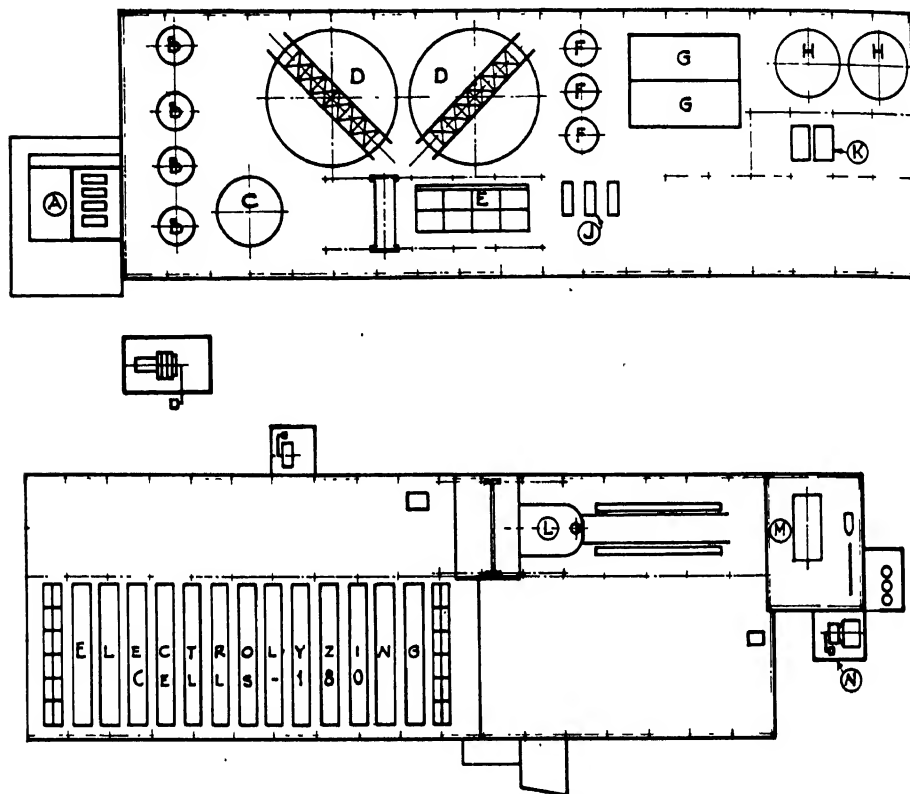


FIG. 2.—LAYOUT OF EQUIPMENT.

A, iron dissolving cells
B, three leaching tanks, one oxidizing tank
C, high acid storage tank
D, 50-ft. thickeners
E, Moore filter
F, three mechanically agitated purification tanks

G, spent-electrolyte storage
H, purified solution storage
J, three Shriver presses
K, heating plant
L, melting furnace
M, motor-generator set
N, air-cooling for motor-generator set

with about 3.0 per cent zinc dust, based on cathodes produced. At times copper sulphate has been used as an addition agent but, in general, better solution has been made without its use.

The purified solution usually contains about 135 grams per liter of zinc, with impurities as follows: Fe, 20 mg. per liter; As, trace; Cd, 1.5 mg. per liter; Cu, 0.4 mg.

In the electrolysis, the acid content of the upper five cells of the cascade is held at 10.0 to 11.0 per cent H_2SO_4 , that of the bottom cell being about 2.0 per cent higher. The zinc depletion is about 80 grams per liter and the zinc content of the cell acid about 55 grams per liter.

Goulac is used as an addition agent in the amount of 1.1 lb. per cascade per day.

It is added to the feed line to the cell room rather than to the individual cells.

Operation of the casting furnace has been very simple and surprisingly efficient. The casting crew works only five days a week. Slabs are cast on the afternoon and night shifts and the furnace is skimmed on the day shift. The dross is worked with a small amount of salammoniac and raked into steel concrete buggies. These are dumped and such liquated metal as is present runs through and freezes on the concrete floor. The metal is picked from the skimmings and returned to the melting furnace. The lumps of skimmings are broken up and screened on a $\frac{1}{2}$ -in. square-mesh sand screen. The undersize is shipped to the retort plant and oversized metallics are returned to the furnace.

With no further treatment than that described above, the ratio of slabs to cathodes has been 95.5 per cent. The zinc content of the skimmings varies between 84 and 87 per cent with less than 0.1 per cent of the cathode zinc unaccountable.

The data in Table 1 are those of December 1941, and are typical of the operation. They are not ideal but they show what has been accomplished in eight months of operation.

TABLE 1.—Data for December 1941

Tons feed treated.....	2,919
Zn, per cent.....	64.16
Pb, per cent.....	1.59
Tons zinc dust used.....	51.2
Based on cathodes, per cent.....	3.32
Tons 60° H ₂ SO ₄ used.....	319
Tons classifier sand.....	107
H ₂ O, per cent.....	16.1
Zn, per cent.....	41.6
Pb, per cent.....	1.16
Tons purification cake.....	159
H ₂ O, per cent.....	25.0
Zn, per cent.....	45.1
Cd, per cent.....	6.4
Cu, per cent.....	5.2
Tons cathodes stripped.....	1,540
Average amperes.....	9,601
Ampere efficiency, per cent.....	88.52
Power consumption, kw-hr. per lb. cathodes, d.c.....	1.419
Load factor.....	93.34
Tons cathodes melted.....	1,608
Tons slabs cast.....	1,550
Ratio slabs to cathodes.....	0.964
Slab assay, per cent:	
Zn (difference).....	99.9950
Pb.....	0.0026
Cd.....	0.0012
Fe.....	0.0009
Cu.....	0.0003
Tons dross produced dry.....	79.3
Zn, per cent.....	84.4
Dross to cathodes melted, per cent....	4.2
Labor, shifts per ton slabs.....	1.80
NH ₄ Cl used, lb. per ton slabs.....	1.55

Electrolytic Zinc at Corpus Christi, Texas

BY GEORGE H. CUNNINGHAM* AND ALLEN C. JEPHSON,† MEMBERS A.I.M.E.

THE plant for production of electrolytic zinc recently erected by the American Smelting and Refining Co. is situated along Nueces Bay, on the Gulf Coast, some 5 miles west by rail and highway from the city and port of Corpus Christi. A ship channel from the port now approaches to within 2 miles of the site. It is expected that this will be extended at some future date and so provide direct water shipment from the plant. In addition to Gulf shipping, an intercoastal waterway connects Corpus Christi with Houston and New Orleans.

Factors leading to the establishment of this plant in the area were: ample supplies of natural gas for the generation of electric power, advantageous shipping lanes, favorable market for acid, adequate supply of labor, and moderate climate.

GENERAL DESCRIPTION

The plant was erected primarily to assist with the production of high-grade zinc much needed for war purposes. Production started during October 1942. The purity of the slab-zinc output meets the American Society for Testing Materials' special high-grade specifications. Other products of the plant are electrolytic cadmium and sulphuric acid. Residues containing lead, copper and silver are sent for treatment to the Company's smelter at El Paso, Texas.

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The design of the plant includes the use of Trail suspension roasting equipment, contact acid equipment, also batch leaching in mechanically agitated tanks, pressure filtering and washing of leach pulp, batch purification in mechanically agitated tanks followed by clarification in filter presses and cooling of purified solution by evaporation. Electrolysis is performed in cells using Tainton alloy anodes and aluminum cathodes. Cathode current density is 60 amp. per square foot. Except for the portion returned to the leaching division, the cell solution is continuously flowing in closed circuit through the cells to cooling towers, which hold cell temperatures within desired limits. Direct current for electrolysis is supplied by generators driven by steam turbines. The cathode zinc is melted in a gas-fired furnace and cast in the usual way into slabs for shipment.

The plant divides into five major divisions: Concentrates Storage, Roasting and Acid, Leaching, Electrolysis, Melting and Casting. No attempt is made to give many tabulated data in this paper; it is mainly a general description of the divisions and methods employed for operation. A plan is shown in Fig. 1 and a general flowsheet in Fig. 3.

CONCENTRATES STORAGE

The original plan for inward shipments was to receive zinc concentrates by steamer at the port of Corpus Christi, there to unload into open railroad cars and move into the plant by rail. Up to the present, however, concentrates have been received mainly in box cars from mines in Mexico.

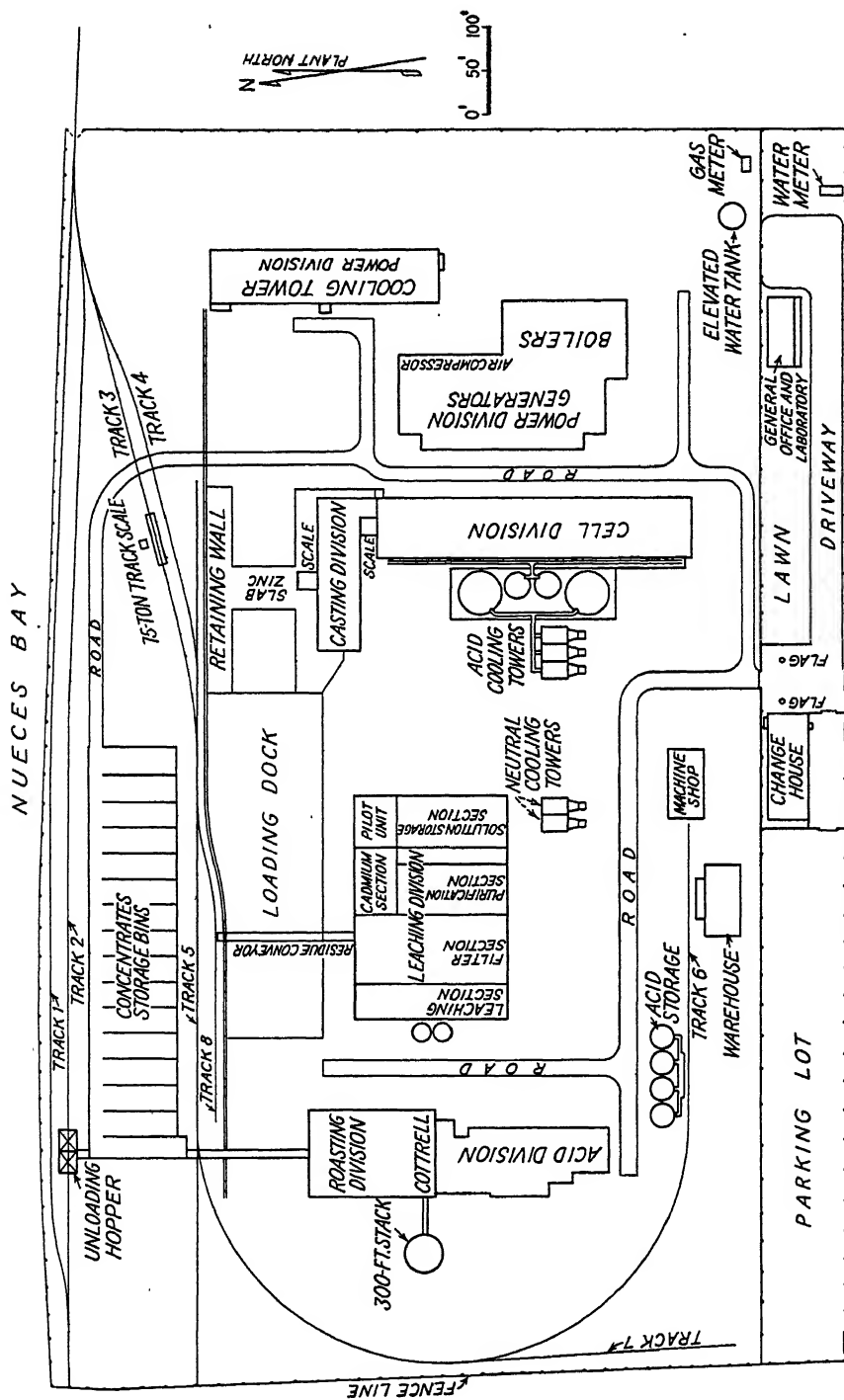


FIG. 1.—PLAN OF ELECTROLYTIC ZINC PLANT AT CORPUS CHRISTI.

The incoming cars are weighed on plant track scales and moved to the unloading track for sampling.

The concentrates are hand-shoveled from

Works Co.). These furnaces are 20 ft. inside diameter, have two upper drying hearths, a combustion chamber 24 ft. high, a third hearth or bottom of combustion



FIG. 2.—CORPUS CHRISTI ELECTROLYTIC ZINC PLANT OF AMERICAN SMELTING AND REFINING COMPANY.

box cars into hoppers from which they are taken to storage by an 18-in. belt-conveyor system.

The concentrates storage consists of 15 bins of 2000 tons capacity each, or a total of 30,000 tons. The bins provide a ready means of storing separately various grades or shipments.

Reclaiming of concentrates from storage is performed by two gasoline-driven shovels of one yard capacity each, fitted with rubber tires. The shovel scoops from the bin and delivers to an 18-in. belt-conveyor system, which in turn delivers to feed bins of 100 tons capacity each in the roasting division. In this belt system there is installed a magnet for removing scrap iron, a disintegrator for breaking up lumps, and a weightometer for recording the weight of concentrates transferred from storage to the roasting division.

ROASTING AND ACID

The roasting and acid division comprises the roasting of the zinc concentrates and the recovery of the sulphur from resultant gases in the form of acid.

Roasting

Concentrates are roasted in two Skinner suspension-type roasters (Colorado Iron

chamber and a lower or fourth hearth from which gases and calcine leave the furnace. The capacity of these furnaces is 70 to 120 tons of concentrates each per day. At starting it took some weeks for operators to work out a system of control, but the units are now running very smoothly.

From the 100-ton wet-concentrates bins above each furnace, a 30-in. feeder belt discharges to No. 1 drying hearth of the roaster. The rabbles of No. 1 hearth move the concentrates inward, as they undergo partial drying, to a center sealed drop, which delivers to No. 2 hearth. On No. 2 hearth the drying is completed and the concentrates rabble outward, discharging down a chute into a ball-mill feed bin. Under average conditions the moisture of concentrates entering No. 1 hearth is 6.5 to 7 per cent; entering No. 2 hearth, 4.5 to 5 per cent and when they reach the mill feed bin, 0.5 per cent or less.

There are two 7-ft. by 36-in. Hardinge air-swept ball mills, one per roaster, each having a capacity on this regrind of 5 tons or more per hour. The ground product is carried by air to classifier in closed circuit with the mill. Each classified product, 98 per cent minus 200-mesh, is air-borne to a 9-ft. cyclone dust collector, which

discharges through an air flap valve into an 80-ton dry feed bin for the concentrates burner.

This bin discharges through a 24-in. gate valve and a closed-type rotary feeder to a 24-in. belt, which feeds the concentrates burner. Air is supplied to the burner by a fan at 15,000 cu. ft. per min., and the fan also draws a controlled quantity of hot gas from the roasting chamber into and across the No. 2 drying hearth. This hot gas, after being used for drying, is discharged back into the roasting chamber through the concentrates burner. A regulated amount of atmospheric air is mixed with this gas after it leaves the No. 2 drying hearth. The quantity of atmospheric air taken into the burner fan is controlled to suit the roasting operation.

Calcine settles on the bottom of the roasting chamber or hearth No. 3, is rabbled to the center and drops to hearth No. 4, where it is rabbled outward and is discharged through a chute to an 18-in. screw conveyor 39 ft. long. Chrome-steel arms and rabblers are used on No. 3 and No. 4 hearths. Dust from the waste-heat boilers, cyclones and Cottrell dust precipitators is returned to No. 3 hearth. Calcine in the screw conveyor is transferred to another 18-in. screw conveyor 70 ft. long. These conveyors are water-cooled both on the shaft carrying the screw and on the jacket. From the screw conveyor the calcine is elevated 44 ft. by a steel chain-and-bucket elevator of 15 tons per hour capacity. The elevator discharges through a chute on a 3 by 5-ft. Hum-mer screen of 20 mesh.

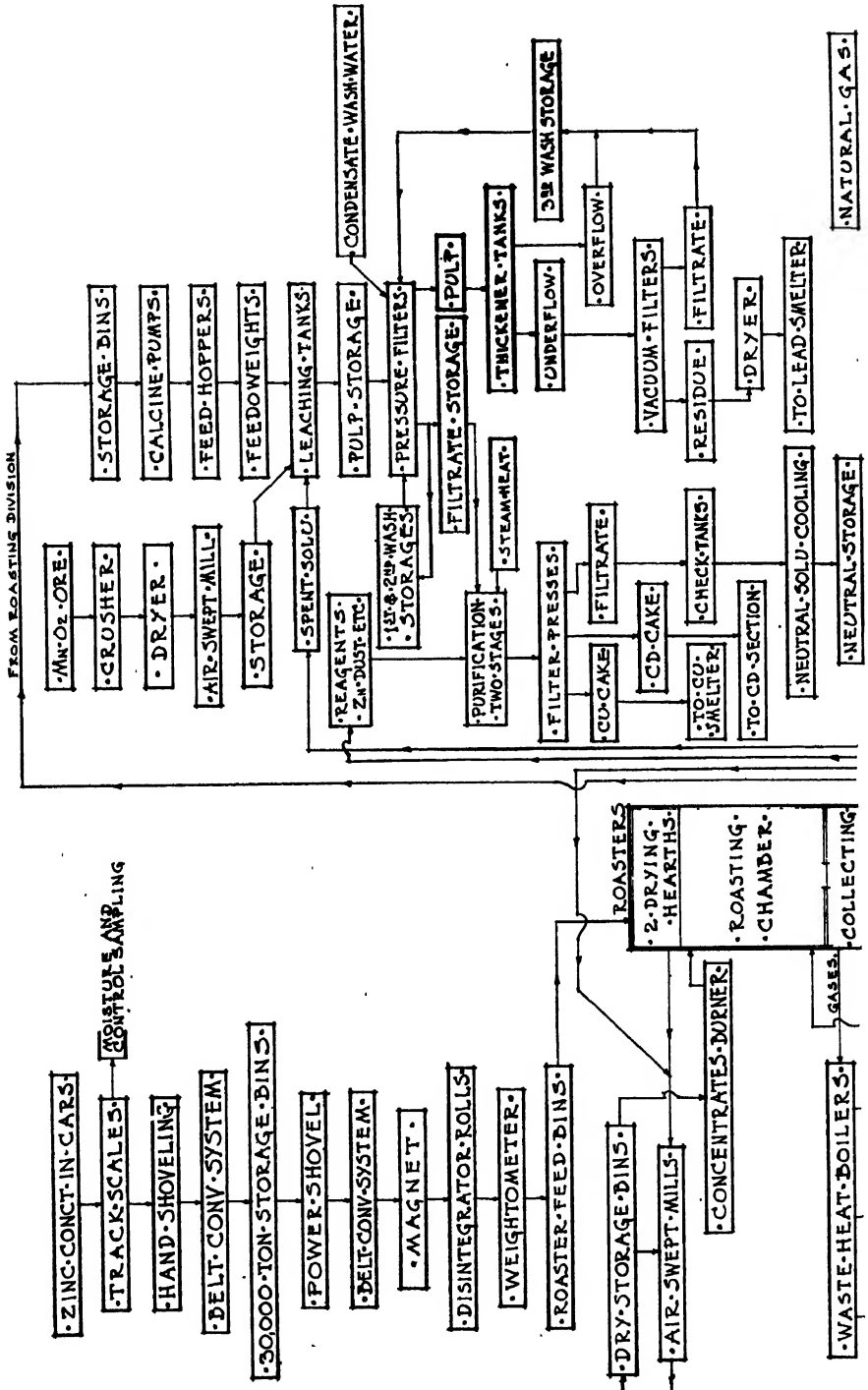
The undersize is sent to the 4-in. Fuller-Kinyon calcine pumps and the oversize may be delivered either to a 5-ft. by 22-in. denodulizing ball mill of 2 tons per hour capacity or, in case of emergency, to a small storage bin, which discharges through a 14-in. rotary valve to the boot of the elevator again. The ball mill discharges through a chute to Fuller-Kinyon pumps,

which carry the calcine through a 4-in. calcine-conveying pipe line 475 ft. long to storage bins at the leaching division or directly to the leaching charge bins.

The long-radius bends in the pipe quickly eroded through from wear of the calcine, but later were lined with concrete to overcome this trouble. Wear on the pump screw is also rather heavy.

Gas from the No. 4 hearth of each roaster is conducted through a short suspended-arch brick flue to a waste-heat boiler. The flue opening at the roaster is 4 ft. 6 in. high by 10 ft. wide. The gases make a single horizontal pass through the boiler and travel in a straight line until discharged into a vertical offtake. Pressure drop through the boilers varies between 0.1 and 0.2 in. These Erie City Iron Works boilers, one to each furnace, are three-drum, 440 boiler-hp. water tube, with a capacity of 6000 to 12,000 lb. steam per hour at 150 lb. pressure.

The steam generated is about 0.7 lb. per pound of concentrate roasted, and is used for solution heating in the leaching division. Gases from each boiler go to separate cyclone units of two each connected in parallel. Gas volume is 8,500 to 10,500 cu. ft. per min. each, at 320°C. maximum gas temperature. The gas is drawn from each cyclone unit through a 36-in. diameter steel flue by a hot-gas fan at 320°C. at the rate of 10,000 cu. ft. per min. Each fan is driven by means of a hydraulic coupling. Its speed may be varied from zero to full speed with infinite adjustments. The gas is delivered through a common steel flue to the two Cottrell dust precipitators, comprising three units each. Rated capacity per precipitator is 18,500 cu. ft. per min. at 260°C. From the Cottrells the gas passes through a 36-in. diameter steel duct to the acid section. The original three-unit Cottrell proved insufficient at increased loads and an additional three-unit Cottrell is therefore being installed.



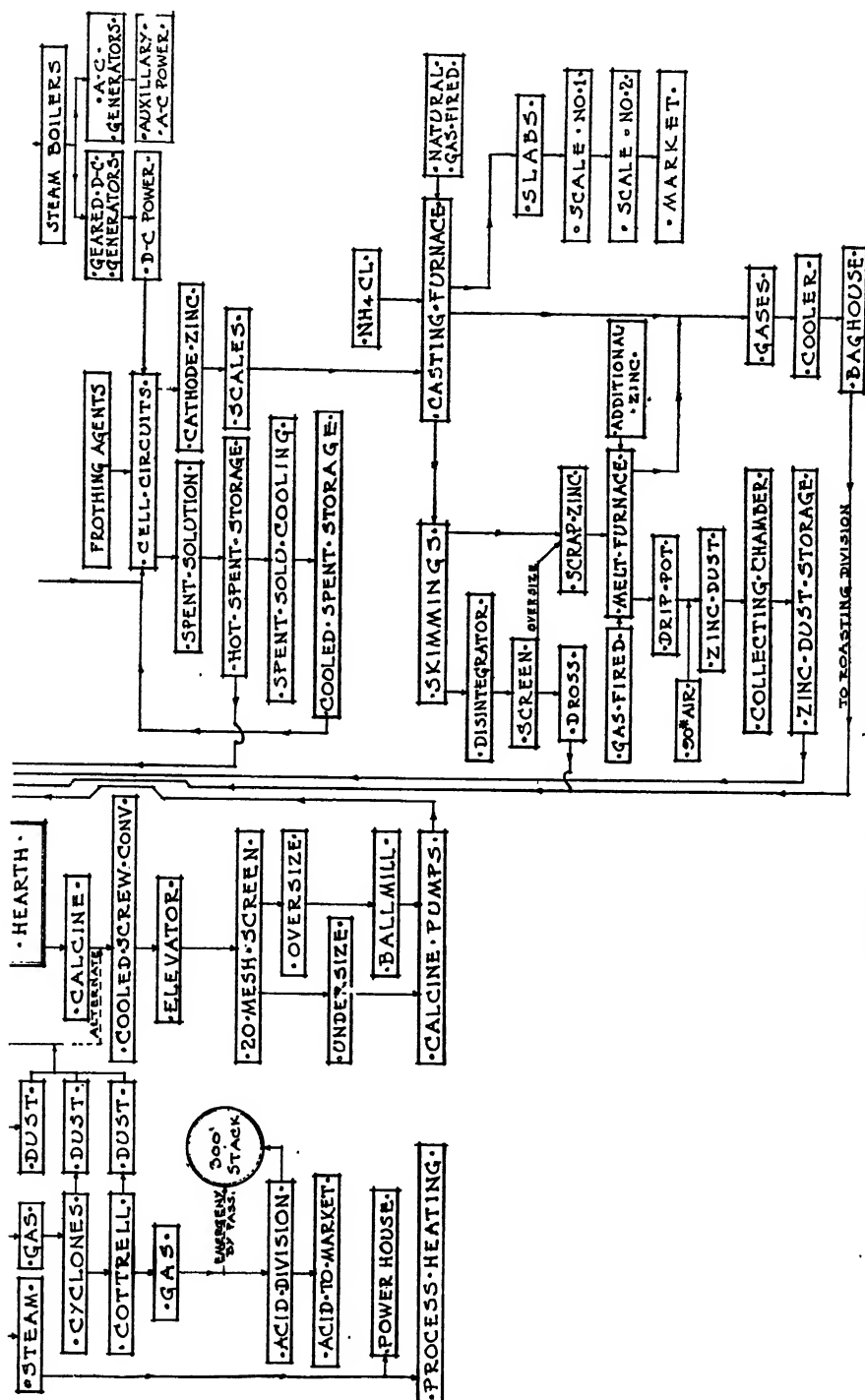


FIG. 3.—GENERAL FLOWSHEET, CORPUS CHRISTI ELECTROLYTIC ZINC PLANT.

All dust, about 35 per cent by weight of the calcine, is handled in a closed system and ultimately returned to the No. 3 hearth of either roaster. Dust from the

drops through a sealed feeder to the same conveyor. Cottrell dust discharges into a 5-in. side-pull Redler conveyor, 1.5 tons per hour capacity, which discharges to

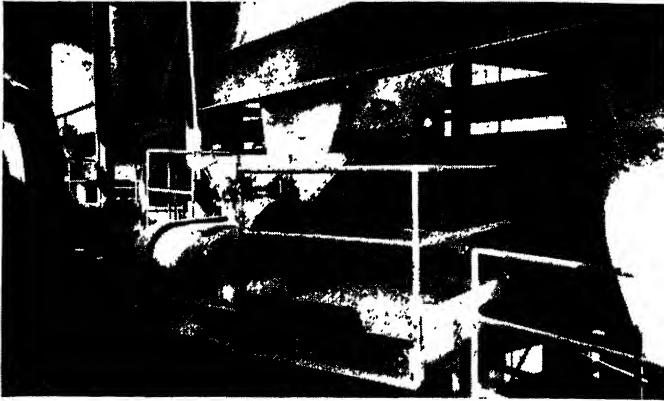


FIG. 4.—SPECIAL TYPE OF WET FEED BINS OVER ROASTER.

waste-heat boilers drops through a hopper to a 10-in. screw conveyor. Cyclone dust

two 10-in. screw conveyors, one for each roaster unit. The screw conveyors are each 44 ft. long and carry the Cottrell, cyclone and boiler dusts to 5-in. L-type Redler conveyor elevators, having a capacity of 3 tons per hour. The Redlers carry the dust 11 ft. horizontally and elevate it 36 ft. to 8-in. screws, which feed through the side of each furnace into the combustion chamber just above No. 3 hearth. When desired, this dust may be sent direct to calcine conveyors.

TABLE I.—*Typical Roaster Data and Analyses*

Tons concentrates roasted in 30-day period.	4,444
Tons concentrates roasted per furnace per day.....	80.1
Percentage of concentrates minus 200-mesh after grinding.....	98
Percentage of SO ₂ in gases at Cottrell inlet.	9.0
Temperature in roaster combustion chamber	930°C.
Temperature of gases entering Cottrell.....	215°C.
Temperature of gases leaving Cottrell.....	208°C.

Constituent	Concentrates, Per Cent	Calcine, Per Cent	Cottrell Dust, Per Cent
Total Zn.....	56.7	66.0	52.7
Acid-soluble Zn.....		64.5	
Water-soluble Zn.....		0.3	
Pb.....	1.3	1.0	2.15
Cu.....	0.57	0.65	0.52
Cd.....	0.71	0.82	1.40
Fe.....	4.60	5.5	4.3
Total S.....	31.5	0.83	6.25
Sulphate S.....		0.73	5.70
Sulphide S.....		0.1	0.5
Insoluble.....	2.3		
As.....	0.11		
Sb.....	0.04		
Mn.....	0.40		
CaO.....	0.51		
MgO.....	0.11		
Moisture.....	6.8		
	Oz. per Ton	Oz. per Ton	Oz. per Ton
Au.....	0.007	0.009	0.01
Ag.....	5.2	5.2	14.0

Typical roaster data and analyses are given in Table 1.

Acid Section

The sulphuric acid section consists of a standard Leonard-Monsanto contact unit. The 9 per cent SO₂ gases, after passing the Cottrell dust precipitator, enter the scrubbing tower at about 208°C. and continue through the mist Cottrell treater, coke box, drying tower, etc., to vanadium mass converters. The water from the scrubbing tower is discharged to a cone-bottom settler, from which a lead sulphate sludge is recovered for shipment. The

overflow from the settler is pumped to a stripping tower at the bottom of which air is admitted. The stripping tower recovers entrained SO_2 in settler water and passes it

through a 12-in. screw conveyor and a Merrick Feedweight to one of the leaching tanks at a maximum rate of 48 tons per hour.

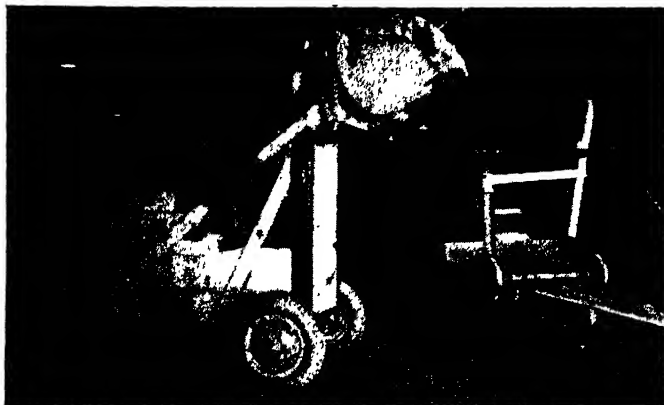


FIG. 5.—GASOLINE SHOVEL FOR CONCENTRATES.

back to the gas main leading into the mist precipitator.

The acid unit was designed to have a capacity of 125 tons of 100 per cent acid daily but has on occasion produced more than that amount. The unit will also produce 25 per cent of the acid output as oleum. There is a storage for 3000 tons of acid. Shipments are regularly made by rail in tank cars.

LEACHING DIVISION

This division of the plant includes the leaching operation, filtering, washing, residue drying, purification, cooling of purified solution, and the production of cadmium. Typical data are given in Table 2.

Leaching

Calcine from the roasting division is generally stored in two bins of 500 tons capacity each, from which it is handled by a Fuller-Kinyon pump to individual 20-ton charge bins over the four leaching tanks. Each calcine charge bin discharges

The leaching tanks are wood-stave construction, measuring inside the lining 20 ft. in diameter by 10 ft. deep. They are lined with 8-lb. sheet lead and 4.5 in. of acidproof brick. Agitation is provided by horizontal wooden stirrer arms attached to a wooden shaft with Worthite bolts. The arms are placed 10 in. above the bottom of the tank. The agitator may be driven at 2, 4, 6 or 8 r.p.m. as desired, by a four-speed 15-hp. motor. Each tank has a one-inch resin-pressed plywood cover and plywood ducts for ventilation.

A leach is started by pumping in 18,000 gal. of spent electrolyte containing 200 grams per liter H_2SO_4 and 50 to 60 grams per liter of zinc. The electrolyte is delivered through an 8-in. diameter lead-pipe line from the cell division. To this is added 1500 gal. of strong wash water from the Burt-filter wash storage. Sufficient calcine is then added to drop the acidity after 2 hr. to 5 to 10 grams per liter. Finely ground MnO_2 ore is added during this first stage to oxidize the ferrous iron in solution, 200 lb. per leach being generally sufficient.

Acidity and ferrous iron are checked at the end of the 2-hr. period, and during the following 2 to 3 hr. the leach is completed by the addition of successively

The interior is fitted with wooden filter boards of triangular cross section spaced symmetrically around the inside circumference and extending half the filter length

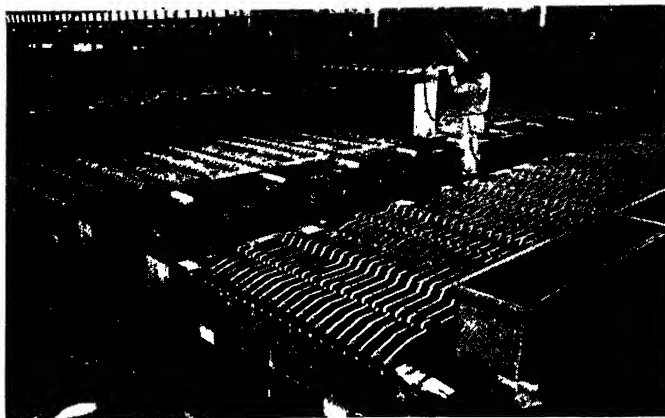


FIG. 6.—ARRANGEMENT OF CELLS, ELECTROLYTIC DIVISION.

smaller amounts of calcine and of MnO_2 if needed. The filtration rate is watched carefully, and the final, very small additions of calcine are governed by the filtration rate rather than by the pH of the solution, once the solution has become neutral to methyl orange.

Each leaching tank is discharged through a 6-in. opening in the tank bottom controlled by a rubber plug with a ceramic seat, and also by a 6-in. rubber-lined valve. The pulp drops directly through a 6-in. rubber hose to pulp storage.

The finished leach is dropped into one of two agitated pulp-storage tanks, which are 27.25 ft. inside diameter by 10 ft. deep and of the same general construction and lining as the leaching tanks. Working capacity of each pulp tank is 40,000 gal. Pulp is pumped from the tanks through a 5-in. copper pipe by 4-in. Worthite pumps, which deliver to the Burt filters through a 4-in. copper pipe header.

There are seven Burt filters, each 5 ft. in diameter by 40 ft. long. Each filter is rotated at a speed of 6 r.p.m. by a 15-hp. motor. The filter shell is steel, copper lined.

from each end, there being a total of 32 boards per filter. The boards are grooved lengthwise on the two exposed faces, in order to facilitate the flow of solution, and are covered with cotton-twill filter bags. Each element has a $1\frac{1}{4}$ -in. bronze discharge nipple projecting through the filter shell at the center of the filter, through which the clear solution passes to be carried by launder system to storage tanks under the filters. The filters are serviced at the inlet ends by 4-in. pulp lines, 3-in. wash-water lines, 2-in. air lines at 45 lb. pressure, 2-in. condensate-water lines, 2-in. steam lines and 4-in. vacuum lines.

The time needed for a complete filter cycle on a full charge is 3 to 4 hr., of which about $1\frac{1}{4}$ hr. is taken by the main filtration, the remainder by charging, three washings, repulping, and discharging.

Filtrate and washes are discharged from the nipples into a lead-lined catch pan. This pan discharges into a copper launder, which may be swung by hand to discharge into either the filtrate launder or one of the wash-water launders. In turn, the filtrate launder discharges into any one of three

storage tanks for impure solution. Rubber plug valves in the filtrate launder control the outflow to each tank.

These tanks are unlined wood-stave construction, 20 ft. in diameter by 8.5 ft. deep, having a capacity of 18,000 gallons.

The wash-water launders discharge into first and second wash storages. The three wash-storage tanks are unlined wood-stave construction, 12-ft. diameter by 8.5-ft. depth, having a capacity of 6700 gal. each, in which are stored strong, medium, and weak wash water.

Filtering

The filtration cycle is started by filling a filter with pulp from the pulp-storage tanks. The filter is then rotated and air pressure is turned on. The clear solution is forced through the canvas covering the filter elements, follows the grooves in the boards and escapes through the discharge nipples. The solids build up on the canvas inside the filter. When the filtration is finished, air and steam escape through the nipples and the pressure inside the filter shows a drop on the pressure recorder. The air is now turned off and strong wash water is pumped in by one of the two 3-in. wash-water pumps, delivering at a rate of 250 gal. per min. When sufficient water has been added, the valve is closed and air turned on again. This enriched strong wash water is discharged to the impure-solution storage.

In similar fashion, one charge of medium wash water is advanced to the strong-wash-water tank, and one charge of weak wash to the medium wash tank. At the end of this third washing, more weak wash, or condensate water, as the case may be, is pumped into the filter and the vacuum is turned on with the filter rotating. After a few minutes the residue and water become a heavy slurry, which is discharged through four ports in the discharge end of the filter into a residue launder. More weak wash water is used toward the end of the dis-

charging period, to flush the remaining residue out of the filter, after which the ports are closed and the filtration cycle is completed.

Solution from the strong-wash-water tank is partly used in the leaching tanks, as previously mentioned. The water thus removed from the wash-water circuits is balanced in the weak-wash-water tank, which receives residue thickener overflow, filtrate from thickener underflow, and condensate water as needed. The bulk of the condensate water used is pumped from the power house into a storage tank, which also collects condensate from the steam-heating coils in the purification tanks.

Drying Residue

The residue discharged from the Burt filters is carried by launder to two Dorr thickeners connected in parallel. The thickeners are 30-ft. diameter by 8-ft. depth, with standard arms rotating at 0.2 r.p.m. The overflow returns to Burt-filter weak-wash storage. The underflow is handled by two Duplex diaphragm iron pumps with a capacity of 100 gal. per min., to two Oliver vacuum filters 8 ft. in diameter by 12 ft. long. The filtrate is returned to Burt-filter weak-wash storage.

The residue cake from the vacuum filters, containing about 50 per cent moisture, is delivered by belt conveyors to a gas-fired rotary drier, 6 ft. in diameter by 35 ft. long and revolving at 6.4 r.p.m. The partly dried residue from the drier contains about 30 per cent moisture. It discharges through a chute to a chain-bucket elevator with a lift of 29 ft., from which it is dropped to a conveyor belt that delivers it 180 ft. away to a hopper over the railroad siding, where it is loaded into cars for shipment to the lead smelter.

The vacuum pumps installed to supply the Oliver and Burt filters consist of two 22-in. by 9-in. horizontal, straight-line, single-stage, double-acting Chicago Pneumatic units, each rated to handle 830 cu.

ft. per min. at 20-in. vacuum. One pump operates continuously for the vacuum filters, the other as required for the Burt filters.

TABLE 2.—*Typical Data for Leaching Section*

Tons calcine leached per day.....	131
Tons calcine leached per leach.....	15.7
Tons MnO ₂ ore used per day.....	0.8
Gallons spent electrolyte per leach.....	18,000
Gallons wash water per leach.....	1,500
Acidity at start of leach, grams per liter.....	200
Acidity after first calcine addition, grams per liter.....	6
Leaching time, hours.....	4 to 5
Ratio, lb. calcine per lb. acid.....	1.07
Burt filtration rate, gal. per sq. ft. per min.....	0.055
Residue produced, per cent of calcine leached.....	23

Analyses	Calcine, Per Cent	Residue, Per Cent
Total Zn.....	66.3	18.4
Acid-soluble Zn.....	64.4	9.5
Water-soluble Zn.....		2.8
Fe.....	5.5	24.0
Sulphate S.....	0.76	
Sulphate S.....	0.1	

Burt Filtrate

Zn, grams per liter.....	175
Cu, grams per liter.....	0.9
Cd, grams per liter.....	1.3
Fe, mg. per liter.....	5
Co, mg. per liter.....	16
As, mg. per liter.....	0.5
Sb, mg. per liter.....	0.3

Purification

Time Cu-Co-As-Sb removal, hr.....	5-6
Time Cd removal, hr.....	4-5
Analysis of purified solution:	
Zn, grams per liter.....	172
Mn, grams per liter.....	5
Fe, mg per liter.....	15
Cu, Cd, Co, As, Sb, Mg per liter or less..	1

Purification

Solution is handled from the three storage tanks for impure solution by 4-in. Worthite pumps, two of which are installed, each rated at 500 gal. per min. The pumps deliver to four purification agitator tanks through 4-in. rubber hoses. The suction lines are 4-in. copper and provided with valves, so that either pump may handle. All purification tanks are covered with 1-in. resin-pressed plywood and are ventilated through plywood ducts connecting with a fan in the building roof.

A two-stage purification of the zinc sulphate solution is employed, the first stage removing the copper, cobalt, arsenic and antimony; the second removing the cadmium. Four tanks operate in parallel for each of the two stages.

The purifiers are wood-stave unlined tanks with inside dimensions of 20-ft. diameter by 10.5-ft. depth, having a capacity of 22,000 gal. These purifiers are equipped with steam-heating coils of 2-in. copper pipe circling close to the tank staves and carried by wooden supports about 16 in. high, which rest on tank bottom. An agitator constructed of 6-in. copper pipe extends to within 9 in. of the bottom of the tank. Agitators are driven at 6 to 12 r.p.m. by a 10-hp. motor. Zinc dust is stored in a four-compartment 10-ton bin on the purification floor. Spent electrolyte is stored in a 3200-gal. lead-lined tank, from which it is distributed as needed through rubber hoses to any purifier tank.

During the first stage of the purification, in which copper, cobalt, arsenic and antimony are removed, spent electrolyte is added continuously, while zinc dust and copper and arsenic reagents are added at intervals. The temperature is raised to 90°C. or higher. The first stage is completed after 5 to 6 hr. and the solution is then pumped through one of two 36-in. bronze Shriver filter presses into one of the four cadmium-removal purifiers by 4-in. Worthite pumps. There are five purification presses having 36 plates, and each is fitted for hydraulic closing by a centrally located high-pressure oil pump. Drip pans under the presses collect leakage solution, which drains to a small tank from which it is returned to a later purification. Kraft paper is used over the filter canvas to ensure a clear filtrate. The copper cake is dropped through chutes into hand carts, which are emptied into an outdoor storage bin for shipment to a copper smelter.

During the second stage of the purification installed for removal of cadmium,

spent electrolyte and zinc dust are added and the temperature is allowed to drop to 75°C. After 4 to 5 hr., the solution is handled by 4-in. Worthite pumps through one of three 36-in. bronze Shriver presses to one of four wood-stave check tanks of the same dimensions and capacity as the purifiers.

To handle solution from each purification stage, a set of three Worthite pumps is provided, two to operate and one as spare, all interconnected so that any pump may be out for repairs. Rubber hoses are used on the ends of delivery lines to give flexibility of discharge and to avoid valves.

The cadmium filter cake from the final filtration is taken to the cadmium section for further treatment.

The purified solution, to which a small amount of spent electrolyte has been added in order to minimize precipitation of basic salts, is stored in the check tanks until the purity of the solution has been checked. Provisions are made for returning for repurification any batch of solution that is found by control checking to be unsatisfactory.

Solution from the check tanks is handled in lead piping by 4-in. Worthite pumps of 500 gal. per min. capacity, two of which are installed. They deliver through a common header either direct to pure-solution storage or first over the cooling tower and then to storage. Cooled solution flows from the tower in a launder which discharges into the neutral storage tanks, or by-passes into two 24,000-gal. sump tanks, from which the solution may be returned to the tower for further cooling when desired. Pure-solution storage consists of three wood-stave, unlined tanks, with inside dimensions of 30-ft. diameter by 10.5-ft. depth, each holding 50,000 gal. The purified and cooled solution is now pumped by two Worthite pumps of 200 gal. per min. capacity to a lead-lined launder 215 ft. long, which delivers the solution to the cell division.

Typical data are given in Table 2.

ELECTROLYSIS

The overflow solution from the 320 cells is collected in two storage tanks for hot spent solution, from which it is pumped over a cooling tower. To the cooled spent solution are added controlled amounts of cooled purified solution from the leaching division. This mixed cell-feed solution is stored in two solution-storage tanks, from which it is pumped continuously to the cell-feed launder system, where reagents are added. The solution then flows in parallel through the cells and is returned to the hot spent storage tanks.

The 320 cells are divided into two electrical circuits, each with 160 cells in series, placed in 16 banks of 10 cells each. Each cell contains 25 anodes and 24 cathodes in parallel. The current path for one circuit is from the positive conductor bar through the anodes and electrolyte to the cathodes in cell 10 of bank 1, through the next 9 cells in bank 1 to the cathode bar at the rear of bank 1, through a connecting bar to the anode bar at the rear of bank 2, through the 10 cells in bank 2 to the cathode bar at the front or stripping-floor end of bank 2, through a connecting bar between banks 2 and 3 to the anode bar at the front of bank 3, etc. The current leaves the unit through the cathode bar at the front of bank 16. Alternate cell banks not connected by permanent bars at the front end are provided with movable cutout bars. By means of these bars 20 cells at a time are cut out for cleaning and repairing.

The cells are constructed of 4-in. reinforced concrete with 8-lb. lead lining; inside, they are 7 ft. long, 2.5 ft. wide and 4.5 ft. deep.

The anodes are cast at the plant from the Tainton silver-lead alloy. They are cast in grid-pattern sheets, which are $\frac{5}{16}$ in. thick, $19\frac{5}{8}$ in. wide and 31 in. long. The lower corners are cut off for 1.5 in. along the bottoms and sides. The grids have $\frac{3}{16}$ -in. square openings. The anode sheet is burned to a head bar consisting of antimonial lead cast around a

copper bar of $\frac{3}{8}$ by 2-in. cross section. An anode lifter and chain block removes 13 anodes at a time from the cell for cleaning. The anodes are spaced on 3-in. centers. Porcelain button insulators are attached to the anode near the bottom corners, to assist in maintaining the correct spacing.

The cathode is a rolled aluminum sheet, $\frac{3}{16}$ in. thick, 21 in. wide, and 36 in. long, welded to a head bar of silicon aluminum cast with lugs for lifting. A cathode lifter raises 12 cathodes at a time from a cell. The lifter with cathodes transfers by overhead trolley to the stripping floor, where zinc is stripped and cathodes are returned to the same cell. The cathode sheets are provided with wooden strips on the vertical edges to facilitate removal of the zinc deposit and also to aid in maintaining equal spacing between electrodes.

A special feature is the contact between the cathode head bars in one cell and the anode head bars in the next cell. This is obtained by a cone-shaped piece of copper with threaded stud, which is attached to a thread tapped in the underside of one end of the cathode head bar. The cone wedges vertically between special milled copper buttons attached to the end of the anode head bars. The special contacts of cathode and anode also form a wedge contact with conductor bars at each end of cell banks. The design of this contact provides for easy and effective cleaning.

Anodes and cathodes are supported on special porcelain insulating blocks placed on top of the cell edges. Electrode head bars fit into grooves in the insulators, and the correct spacing between electrodes is thus made positive.

In the stripping operation, every other one of the 24 cathodes in a cell are removed at one time and placed in a stripping rack so designed as to make both faces of each cathode readily accessible. The 24-hr. zinc deposits are easily removed by the use of a stripping knife and a mallet. The zinc sheets are stacked in racks, from which they are picked up by a Baker

gasoline-electric truck fitted with a lifting fork. The zinc is carried to scales, weighed and then taken to the charging platform at the melting furnace.

Solution Flow

The two wood-stave lead-lined cool storage tanks are 50 ft. inside diameter by 10.5-ft. depth and have a capacity of 150,000 gal. each. Condensate water is added here when needed to adjust the gravity of the electrolyte. Three Worthite 6-inch pumps, rated at 1500 gal. per min. each, pump the solution to the main cell-feed launder, which extends the full length of the cell room. The conditioning reagents are added at the center entrance to this launder. The solution then flows into 32 individual feed launders, one for each bank of cells, from which each cell receives solution at a regulated rate of about 10 gal. per min. A by-pass allows any excess of solution in the main feed launder to be returned to the hot spent storage.

The cell overflow is collected in individual launders for each bank of cells. These discharge through a main return launder into the two wood-stave lead-lined hot spent tanks, which are 30-ft. inside diameter by 10.5-ft. depth and have a capacity of 55,000 gal. each. From the hot spent storage, two Worthite 6-in. pumps, rated at 900 gal. per min. each, deliver solution to the leaching division through an 8-in. diameter lead-pipe line. Three other Worthite 6-in. pumps, rated at 1500 gal. per min. each, handle the hot spent solution to the three-section cooling towers, from which it returns to the cool storage for recirculating to the cells. The total volume of solution in the cell circuit is about 350,000 gal. About 40,000 gal. of water per day is evaporated from the cooling tower.

Anodes and cells are cleaned at regular intervals. The anodes are scraped, brushed, straightened and repaired as necessary before being replaced. A vacuum cleaning system is used to remove solution and sus-

pended manganese slime from the cells. Vacuum is supplied by a 15-hp. Nash vacuum pump with bronze rotor and cone. Suction is applied through a moisture trap and a 45-ft. barometric leg to a lead-lined steel receiving tank, 8-ft. inside diameter by 8-ft. depth, tightly sealed. The lining is homogeneously welded to the steel, to prevent collapse of lead under vacuum.

When in use, the vacuum system is connected by a lead-pipe line to a 2-in. non-collapsing rubber hose with suction nozzle inserted. This hose is extended to the bottom of the cell being cleaned and the mixture of solids and solution is drawn through the line into the receiver. The mixture is then pumped out of the receiver by a 2-in. Worthite pump and delivered to two elevated storage tanks. These tanks are lead-lined wood-stave, 15-ft. inside diameter by 10.5-ft. depth, and have a capacity of 13,000 gal. each. Air agitation is provided to keep solids in suspension until the sludge is discharged by gravity through a 3-in. lead-pipe line to the suction of 6-in. Worthite pumps handling hot spent solution to the leaching division.

The main bulk of the solids is cleared from the cell by the vacuum system and completion of cell cleaning is performed by scraping caked sludge from sides and bottom and shoveling it into carts for removal.

A froth is maintained at all times on the solution surface of the cells by the use of frothing agents, added by two small cup-type feeders. This froth largely eliminates the mist caused by the escape of gas bubbles formed during electrolysis.

The power for electrolysis and for auxiliaries throughout the plant is developed from steam generated in three Erie City Iron Works boilers fired with natural gas. The direct current is supplied by five Westinghouse direct-current generators of 2500-kw. capacity, which are geared to steam turbines. Auxiliary power is supplied by two Westinghouse alternating-current turbogenerators of 2000 kw. each. Marley

towers with induced draft are used for cooling condenser water. The switchboard and circuit-breaker equipment are General Electric.

The following data are typical of a semimonthly period during 1943:

Zinc cathodes produced, tons.....	1,331
Total current, amp. per circuit.....	10,800
Average volts at power house per circuit..	472
Average current efficiency, per cent.....	84.7
Average kilowatt-hours per pound zinc...	1.48
Average current density, amp. per sq. ft..	60
Temperature of electrolyte, deg. C.....	36

Typical spent electrolyte analyzes: H_2SO_4 , 200 grams per liter; Zn, 56 grams per liter; Mn, 5 grams per liter; Cu, Cd, Co, AS, Sb, Pb, 1 mg. per liter or less.

MELTING AND CASTING

The weighed cathode zinc is transferred from the stripping-floor level with the gasoline-electric truck into a 140-ton gas-fired reverberatory furnace with a flat suspended-arch top. The inside dimensions of the furnace are 12 ft. wide by 21 ft. long by 2.3 ft. average depth of metal bath.

The oxide fume in the furnace gases is recovered in a baghouse after the gases have been cooled in a pipe cooler. This cooler contains 16 vertical pipes about 13 in. in diameter by 20 ft. long, providing a cooling surface of 1120 sq. ft. A fan with the capacity of 12,000 cu. ft. per min. at 200°F. maintains a pressure of about one inch water at the baghouse. The bag chamber is about 30 ft. long by 14 ft. wide by 41 ft. high, and contains 84 bags, used alternately in sections of 42 bags. Bags are 18 in. in diameter by 25 ft. long. They are shaken at 8-hr. intervals.

Molten zinc is removed from the furnace in two 500-lb. capacity ladles and poured into molds placed on two parallel benches opposite the two dipping wells. The benches have 40 molds each. After skimming, the slab zinc and molds are chilled by spraying the underside with water carried through the pivot pipe shaft holding the molds to the bench. After dumping, the 50-lb. zinc slabs are piled in 4000-lb. stacks, which are

taken by a Baker gasoline-electric forked truck to two print-weight scales for double weighing. The slabs are then trucked to the shipping platform and stacked in lots of 50 tons. In addition to this check weighing of lots, the zinc, when shipped, is weighed over the railroad scales.

The slab zinc produced is well over 99.99 per cent in purity.

The casting furnace is drossed once each shift. An hour before drossing time, ammonium chloride is shoveled through the three dross doors on each side of the furnace and the arch temperature is raised to 800°C. from its normal 700°C. Dross is raked into carts holding about 800 lb. and wheeled to a hand-sorting platform for removal of scrap zinc, which is taken to the zinc-dust furnace. The melting efficiency at present is about 95 per cent. The sorted dross is fed to a 15 by 8-in. hammer pulverizer discharging to a 30 by 60-in. vibrating screen with $\frac{1}{8}$ -in. openings. Dust from the pulverizer and screen is piped to the baghouse, and undersize dross is sent to the roasting division. Oversize dross is again passed through the pulverizer and screened, the undersize going to the roasting division and the oversize to the zinc-dust furnace.

The furnace used to melt metal for zinc-dust production is a small reverberatory, the fume from which also goes through the pipe cooler to the baghouse. Metal for dust production is tapped into a tilting ladle and elevated by electric hoist for discharge to a graphite drip pot, 16 in. inside diameter by 15 in. deep. The bottom of the crucible is fitted with a tapered carbon plug having a central hole of about $\frac{3}{64}$ in. in diameter, through which the molten zinc drips. Air at 90 lb. pressure is blown horizontally through an atomizing nozzle against the vertical stream of zinc to form dust.

Atomized zinc is collected in a settling chamber 11 ft. long by 6 ft. wide by 17 ft. high, which has bottom discharge into a 6-in. screw conveyor transferring the dust

to an 8-in. belt elevator carrying 6 by 4-in. buckets, which elevates the dust 27 ft. and discharges through a chute to a 20 by 30-in. Hummer screen. Oversize is used as coarse dust for solution purification. The undersize is stored in a 50-ton bin that discharges through a 14-in. rotary valve to carts by means of which the dust is transferred to the leaching division.

CADMIUM BY-PRODUCT

The cadmium section of the leaching division receives for treatment the precipitate from the second stage of zinc sulphate purification. The cadmium is leached from this precipitate and, after various separation steps, a cadmium sulphate solution is electrolyzed to produce electrolytic cadmium, which is then melted and cast into marketable shapes. All solution tanks in this section are round and of wood-stave construction. When sizes are given, they refer to inside measurements.

Given in more detail, the press cake and cleanings from the second-stage zinc-solution purification tanks are leached with fresh strong acid and return cadmium electrolyte in a wood-stave lead and brick-lined tank, which is 15-ft. diameter by 10.5 ft. deep, and has a working capacity of 12,000 gal. This and all other agitator tanks in the cadmium section are covered and ventilated. The wooden agitator of the tank rotates at 15 r.p.m. After 12 hr. agitation, the cadmium and zinc are taken into solution. The present practice is to make two 12,000-gal. leaches per week.

Leaches are discharged through a 2-in. Worthite pump of 150 gal. per min. capacity to a hand-closed 36-in. bronze Shriver press with 24 plates. The cake from this filtration, containing copper, is stored for shipment. The filtrate, containing about 120 grams per liter of cadmium and 110 of zinc is pumped to an unlined 15-ft. diameter by 10.5-ft. deep sponge-precipitation agitator tank having 14,000 gal. capacity. The agitator rotates at 8 r.p.m. and is placed well above the tank bottom

to provide space for a large quantity of cadmium sponge.

Sponge precipitation is carried out in three stages: (1) enrichment of the unwashed high-zinc sponge left from previous batch, precipitation by several hours' agitation, filtering off the solution to a holding tank, washing and removing sponge; (2) return of the solution, addition of fresh cake from zinc plant with enough zinc dust to precipitate about half the cadmium, filtering off the solution a second time to the holding tank, washing sponge and removing; (3) return of the solution and final complete precipitation of cadmium with excess zinc dust, leaving the sponge for the following batch.

The cadmium-free solution is then pumped through a filter press to the cobalt-purification tank of the same specification as the sponge tank, except that the agitator revolves at 15 r.p.m. By means of the usual reagents, the cobalt content of the solution is lowered to 10 mg. per liter or less. The filtrate from filter pressing is sent to zinc leaching and the cake is shipped with the zinc residues.

The sponges when washed contain an average of below 5 per cent zinc, and are now placed in five steam-heated drying pans, for oxidation prior to leaching with cadmium spent solution. About five days is required to oxidize the sponge sufficiently for satisfactory leaching.

Sponge leaching is performed in two lead-lined tanks, 8 ft. in diameter by 8.5 ft. deep, having a capacity of 3000 gal. each. The wooden agitators rotate at 15 r.p.m. Cadmium spent solution, strong sulphuric acid and condensate water are added to dissolve the sponge. The leach is filtered in a 36-in. bronze Shriver press having 24 plates. The filtrate is delivered to two lead-lined cell-feed tanks of 3000 gal. capacity each, which discharge by gravity to the cadmium-cell feed launder, where it mixes with circulating spent solution and glue solution. Cadmium-cell

overflow solution flows by launder to two lead-lined spent-solution storage tanks of 3000 gal. capacity each. From these tanks it is pumped, part going to a small cooling tower and then returned to the cells, and part to various tanks where it is used for cadmium leaching and acidification. The cooling tower may be by-passed if desired and the recirculated cadmium spent solution sent directly to the cell-feed launder.

There are 10 cells of the same size and construction as those used in the zinc plant. The anodes are solid sheets of chemical lead and the cathodes are aluminum, as in the zinc plant. Both are fitted with wooden strips. Current is supplied by a 50-kw. motor-generator, which delivers 2000 amp. at 25 volts. Current density is 10 amp. per square foot.

Cathodes are stripped every 12 hr. They are folded into bundles, washed and dried. When dry they are melted in an iron pot under a rosin flux. The metal is cast into balls and ingots, weighed and boxed for shipment.

Dross from the melting operation is hand-screened through $\frac{1}{8}$ -in. openings. Undersize is treated in the sponge leach tank; oversize metallics are returned to the melting pot.

Typical analyses are given in Table 3.

TABLE 3.—*Typical Analyses of Cadmium Cell*

Product	Cd	Zn	H ₂ SO ₄
Cadmium cake from zinc plant, per cent.....	20	55	
Leach residue, per cent.....	1	10	
Cadmium sponge, per cent.....	80	5	
Cell-feed solution, grams per liter	200		
Spent electrolyte, grams per liter	100	30	120

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Adherence of Electrodeposited Zinc to Aluminum Cathodes

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(New York Meeting, February 1938)

ONE of the most important contributions to the art of electrolytic zinc production has been the aluminum cathode. This has been used in all major production since its commercial development in 1916. The literature is replete with important contributions, some of which may have been replaced by better ones, but thus far there appears no other metal to take the place of aluminum as cathode material. Credit for this innovation goes to Sherard Cowper Coles, of England. When experimenting on the extraction of zinc from Broken Hill ore at Hayle, Cornwall, in 1893, he introduced the aluminum cathode, and in 1895 obtained British Patent No. 20073.

The reason for this dominant position of aluminum as cathode material in zinc sulphate electrolytes is its unique surface, to which electrodeposited metals usually do not tightly adhere. The metal must be of high purity for best results.

It is possible to develop a starting-sheet method by which thin electrodeposited sheets of cathode zinc are made and stripped from a smooth aluminum plate. Such thin sheets of cathode zinc may be used as are the copper sheets in standard electrolytic copper-refinery practice. However, complications arise because of extreme warping of the zinc starting sheet after a few hours of deposition, and thus special arrangements must be made to compensate for this abnormality.

Reasons advanced for the ease with which deposits may be stripped from the aluminum surface are: (1) presence of a permanent oxide coating on the metal, (2) failure of aluminum to alloy with the deposit, (3) differences in coefficient of expansion, (4) high position of aluminum in the electromotive series of metals. Of these reasons for nonadherence, which may have some application in general deposition, probably the oxide coating has the greatest bearing on the subject of zinc deposition.

Adherence of zinc deposits has occasionally had serious effect on tonnage and production costs. Opinions have differed as to the specific

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cause of this adherence, but most of the ideas on this subject are associated with some degree of corrosion. Experimental work was undertaken by the authors, to confirm or establish several of the causes and to express this tendency to adhere in a relative, quantitative manner. This experimental work, which is the basis of this paper, was done during the years 1934 and 1935, but the actual writing of a report has been delayed until the present time.

An excellent account of adherence of deposits is given by Stimmel, Hannay and McBean,¹ which deals with the subject on a plant scale. Corrosion of the aluminum plate due to a small amount of hydrofluoric acid in the electrolyte was believed to be the chief cause of this adherence, although other causes of corrosion had a modified effect. Several methods were developed at this plant for control of the adherence; for example, application of a slurry of ground anode scale to the aluminum plates, and also a short immersion interval of the aluminum plates in the electrolyte before electrical contact was made.

When a new rolled aluminum plate is used as a cathode, there is generally a lack of adherence until sufficient roughness has been developed on the surface. When adherence does occur, usually it is after the aluminum plate has been in service for a period of time. Thus the subject of age is pertinent to this problem.

In order to measure quantitatively the effort required to pull zinc deposits from aluminum surfaces having various degrees of abnormality, the following method was used: The aluminum surface was covered with chlorinated rubber except for a strip $\frac{3}{8}$ in. wide by 2.8 in. long, which received the deposit. After deposition, one end of the deposit was loosened and the plate anchored face down in a horizontal position. The loose end of the deposit was clamped to a small receptacle into which test lead was poured until the load was sufficient to pull off the deposit. The weight of the receptacle plus the test load represents the stripping load. A similar method of detaching deposits is described by P. A. Jacquet² in his work on the adhesion of copper deposits.

It may be deduced that the complete loss of oxide from the aluminum cathode surface is not likely to occur in regular electrolytic zinc practice because of exposure to air and other oxidizing environment. Theodore Ledin³ and Harold K. Work⁴ have described high-metal dip solutions used to condition aluminum for reception of permanent electroplates. These effective dip solutions contain hydrochloric acid and iron, or hydrochloric acid and cadmium. When the aluminum plate is dipped into either of these solutions the acid dissolves the oxide coating and either the iron or the cadmium is plated securely to the aluminum by the immersion. The aluminum surface is thereby sealed from oxygen attack. Regular deposi-

¹ References are at the end of the paper.

tion thus is made on this strike. In customary zinc practice, the opposite conditions exist as previously noted, hence such cause of adherence must be at a minimum.

There are, however, at least two causes of adherence: viz., partial sealing off of the aluminum surface by impurities and etching of a roughened surface.

EFFECT OF IMPURITIES

Three aluminum plates $\frac{1}{8}$ in. thick, 3 in. wide, 4 in. long of varying degrees of hardness (60, 80 and 115 Rockwell B, no load) were used. Chlorinated rubber covered the surfaces except for a strip $\frac{3}{8}$ by 2.8 in., as previously noted. All plates were conditioned as follows: Cathodically cleaned 5 min. in caustic soda and sodium cyanide solution (15 grams per liter NaOH, 15 grams per liter NaCN), etched for 15 sec. in HF plus HCl solution (300 c.c. 52 per cent HF, 50 c.c. 39 per cent HCl, 300 c.c. distilled water) washed, steel-brushed in running water and immersed in water until the start of electrolysis.

The electrolytic deposition was standardized to 15 hr. operation at 35 amp. per sq. ft., temperature 30° C. The electrolyte contained 80 grams H_2SO_4 ; and 46 grams Zn per liter, as $ZnSO_4$, but no addition agents. Consistent checks in the stripping load for each of the various tempers of aluminum plates were not anticipated, but there was a fairly uniform trend in this load which decreased with increase in hardness of plate.

An aluminum plate that permits easy stripping of the deposit will show a load of 25 to 125 grams for the strip in question. Increases in this load, particularly large increases, demonstrate that the aluminum surface has become abnormal.

After the first conditioning, the average stripping loads were: 75 grams, 50 grams and 40 grams for the soft, medium, and full hard plates, respectively. Several check operations confirm these figures.

Following these series of experiments in commercially pure solution, copper sulphate was added to the electrolyte to give a concentration of 0.011 grams Cu per liter. With this addition, the stripping loads for the second cycle of electrolysis increased to the following average load in grams: 225; 120; 80. Several check operations gave slightly higher loads.

The aluminum plates were then exposed to a copper strike in a copper cyanide solution, 5 min. at 10 amp. per sq. ft., followed by the zinc deposition solution containing 0.011 grams per liter Cu. The average stripping loads were as follows, in grams: soft aluminum plates, 350; medium tempered plate, 350; full hard plate, 210.

A similar experiment was made substituting acid copper sulphate for the cyanide. The results were as follows, in grams: soft aluminum plate, 909; medium tempered plate, 1015; full hard plate, 620.

The stripped deposits contained all of the original copper strike, which was plainly visible on the zinc. The aluminum plates showed no copper by the H_2S test.

The influence of fine copper wire, attached to the aluminum plates just above the level of the electrolyte, was tested in the electrolysis of a commercially pure acid zinc sulphate solution. This "copper wire" test was planned to check observations made several years ago in an electrolytic zinc plant, the high-acid cells of which operated under unusual conditions. In these cells the zinc concentration was 14 grams per liter Zn, and the acid 125 grams per liter H_2SO_4 . The only exposed copper in the cathode assembly was two rivets. Directly below these rivets, extending down for about one-third of the immersed cathodes, there were corrosion areas on the aluminum plate to which the zinc deposits adhered tightly. There is a greater volume of spray from the surface of this solution, and the latter is more active chemically than the usual zinc sulphate electrolytes. Although copper is permissible above the electrolyte in some plants, there are conditions when it becomes adverse, and can cause adherence. The problem was solved by encasing the copper rivets with lead. This copper wire was exposed to the atomized electrolyte. The stripping loads for the second deposition under this condition was approximately the same as the previous high loads stated.

The aluminum surfaces were cleaned with a bristle brush in running water and retested in commercially pure zinc sulphate electrolyte. The average stripping loads under this condition were as follows (grams): soft aluminum plate, 125; medium aluminum plate, 107; full hard aluminum plate, 85.

The increased stripping loads in detaching the zinc deposits obtained by electrolysis of commercially pure solutions are caused by the slightly increased roughness of the aluminum surfaces developed by frequent stripping during the previous tests.

The influence of cadmium on stripping loads was next investigated. A 5-min. cadmium strike deposit was applied in an acid cadmium sulphate solution followed by the usual zinc deposition. The stripping loads were not as great as in the copper strike. However, they were much greater than the loads required to detach zinc deposits obtained from commercially pure solution. Examples of the influence of cadmium show the following stripping loads: soft aluminum plate, 130 grams, 267 grams, 445 and 410; medium tempered aluminum plate, 140 grams, 167 grams, 372 and 155; full hard tempered aluminum plate, 90 grams, 50 grams, 197 and 140.

In nearly all cases the aluminum plates after stripping showed the presence of cadmium by the H_2S test.

The aluminum plates were tested in regular acid zinc electrolyte to which 0.05 gram Cd per liter had been added, but without the cadmium

strike. The average stripping loads were as follows for the second cycle of electrolysis (grams): soft aluminum plate, 250 and 350; medium tempered aluminum plate, 155 and 275; full hard tempered aluminum plate, 140 and 190.

The aluminum plates were then cleaned from all adhering cadmium by immersing in sulphuric acid solution, 70 grams per liter H_2SO_4 , bristle-brushed in running water and again tested in commercially pure acid zinc electrolyte. The average stripping loads were as follows (grams): soft aluminum plate, 142; medium tempered aluminum plate, 125; full hard tempered aluminum plate, 112.

Although the influence of cadmium does not appear decidedly adverse, it does cause irregular and greater stripping loads than occur with the commercially pure solution.

The presence of copper and cadmium in conventional electrolytic operation is so minute that the cause of adherence cannot be ascribed to these metals. Under abnormal conditions, which cause the resolution of the zinc, the aluminum cathode may become etched, and ultimately the surface may develop adherence.

Silver and mercury-strike coats on aluminum plates, followed by regular zinc deposition, also cause adherence. These metals are irrelevant to the subject because they are not present in the solution. However, it appears that some metals, other than copper and cadmium, adversely affect stripping.

ADHERENCE OF DEPOSITS CAUSED BY ETCHING OF ALUMINUM PLATE

The surfaces of the plates were conditioned as follows: Cathodically cleaned in caustic soda and sodium cyanide solution (15 grams per liter NaOH , 15 NaCN), etched 15 sec. in HF plus HCl solution (300 c.c. 52 per cent HF , 50 c.c. 39 per cent HCl , 300 c.c. distilled water), washed, steel-brushed in running water and kept immersed in water until the start of the etching and electrolysis. The plating conditions were the same as stated before. Four new aluminum plates were used for each etching test. The following etching reagents were used: caustic soda (75 NaOH per liter), ammonium zinc cyanide (ZnO , 22.5 grams per liter, NaCN , 37.5; NH_4OH , 33.0; sp. gr., 0.90), zinc-sulphuric acid solution (100 grams per liter H_2SO_4 , 30 Zn).

Table 1 shows the average stripping load per plate for various etchings. Aluminum plates No. 2SH; 113 Rockwell hardness; room temperature; four new plates used for each test. Before etching, the average stripping loads were approximately 10 grams, 30 grams, 12 and 60 grams.

Progressive etching of the plates used in tests IX and X finally produced surfaces from which the deposits could hardly be removed. This procedure is equivalent to the etching of an "old" plate.

A special etching solution of HF and HCl was prepared as follows: 300 c.c. of 52 per cent HF, 50 c.c. of 39 per cent HCl, 300 c.c. of water. Two new No. 2SO aluminum plates, conditioned as previously stated, were dipped into this special etching solution for two minutes, washed and bristle-brushed in running water. The average stripping loads detaching the deposit of zinc were irregular, amounting to 225 and 125. Two more complete etching and plating operations in this solution were applied to these plates, resulting in a stripping load of practically zero.

TABLE 1.—Average Stripping Load per Plate

Test No.	Etchant	Time of Etching	Average Stripping Loads after Etching, Grams			
I	NaOH	20 min.	12	35	10	75
II	NaOH	3 hr.	630	950	985	1100
III	Ammonium cyanide	4.5 hr.	935	700	825	1000
IV	Acid zinc sulphate	9 hr.	842	710	810	690
V	Acid zinc sulphate	11 hr.	800	830	720	750
VI	Acid zinc sulphate	11 hr.	990	970	1120	1025
VII	Acid zinc sulphate	11 hr.	1100	1200	1150	1250
VIII	Acid zinc sulphate	11 hr.	1050	1100	1250	1270
IX	Acid zinc sulphate ^a		1300	1350	1325	1400
X	Acid zinc sulphate ^b		1400	1450	1500	1450

^a Represents plates used in test VIII etched 3 hr. longer.

^b Represents plates used in test IX etched 3 hr. longer.

A vigorous etching does not appear to be as effective as a prolonged mild attack on the aluminum plate.

A straight sulphuric acid etching of an aluminum plate without previous roughening of the surface does not produce adherence of the deposit. The adherence of deposits to the plates is most favored by a slow etching of the *roughened surface*. A small amount of hydrofluoric acid in the acid zinc sulphate electrolyte is particularly harmful.

After a plate has reached the stage when the adherence of deposits has reached a maximum, there are myriads of angular pits, ridges, sharp longitudinal troughs and similar abnormality of texture upon which the deposit can more effectively secure definite anchorage. This abnormality is experienced occasionally in practice when old aluminum plates are exposed for a long time to the action of acid electrolyte. Short periods of deposition at moderately high current density and high current efficiency are favorable factors in nonadherence of the zinc deposit to the aluminum plate.

It was found that the aluminum plates that had developed great adherence would lose most of this adherence if the surface was polished with steel wool. The wool apparently cuts down the aluminum surface and minimizes or removes the angular pits, channels, etc., and gives to

the surface a mirrorlike texture. The steel-wool fibers that were broken during this polishing were removed from the plate. It was found, also, that if the abnormal aluminum surfaces were rubbed with fine carborundum powder the surfaces were greatly altered and deposits made upon these new surfaces had much greater adherence than before. Examples of these features are given in Table 2.

TABLE 2.—*Adherence after Treatment*

Plate No. ^a	Stripping Load, Grams	Polished with Steel Wool. New Deposit Stripping Load, Grams	Rubbed with Fine Car- borundum. New De- posit Stripping Load, Grams
1	800	265	
2	830	50	
3	720		1140
4	750		1125

^a Aluminum plates made adherent by etching (No. 2SH).

Examples of this nature show that if an impurity on the plate is of such character that it will be retained by the plate after the latter has been rubbed, the normal aluminum surface becomes altered, and the stripping characteristics then are influenced by a new surface developed by this impurity.

A variation in the method of conditioning the plates will occasion a variation in stripping load, and frequently a wide variation in results. For example, if a plate is reasonably normal as to texture, the stripping load will be less if the plate is thoroughly dried before being placed in contact with the electrolyte in the cell. There is a pronounced indication that high current density is favorable to nonadherence.

SUMMARY

Although some impurities in the solution, which are plated with the zinc, may increase the stripping load for the removal of deposits, this feature is not regarded as pertinent to the subject of adherence because the purification system will prevent the presence of these toxic substances.

Impurities in solution that promote resolution of the deposited zinc in the acid electrolyte, as well as abnormal etching of the aluminum cathode, maybe the starting point of adverse roughening of the aluminum plate. This roughened surface becomes more etched and hastens the time when the zinc deposit starts to adhere more tightly. The exposure of an old (and usually roughened) aluminum plate to the attack of acid, aided by the absence of zinc, definitely etches it. The partial cathodic zinc protection of the aluminum plate is not sufficient to prevent the development of the adverse surface. The aluminum plates that are hardest develop adverse surfaces at a slower rate.

Mild etching of a smooth aluminum plate does not produce great adherence of deposits. Steel brushing or scratching alone produces a similar effect. Etching of a steel-brushed plate, or etching of a roughened plate caused by prolonged use as a cathode, develops a surface to which zinc deposits will tightly adhere.

Numerous photomicrographs of the aluminum surfaces and cross sections, showing the basic metal and deposit, were made. These show the expected order of the work, do not add to the written description, and therefore have been omitted from the paper.

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Beneficiation of Arkansas Bauxite

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(New York Meeting, February 1944)

THE Bureau of Mines has been charged by Congress to investigate processes for the production of alumina from low-grade bauxite, alunite, and clay. As one part of the program, an investigation of the application of ore-dressing methods to improve the grade of high-silica bauxite is in progress at the Mississippi Valley Experiment Station at Rolla, Mo. This paper summarizes data obtained so far and presents detailed results of tests on four typical samples.

MINERALOGY OF BAUXITE

The name bauxite originally was used to designate the dihydrous aluminum oxide ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). The designation has been retained, although the existence of a specific mineral of such composition has been disproved. The term is now applied to ores of aluminum consisting of various mixtures of the minerals gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), diaspore ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$), and boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$). The predominant hydrous aluminum oxide in most American bauxite, however, is gibbsite.

In some instances bauxite may be amorphous mixtures of the hydrous aluminum oxides that approximate the composition of dihydrous aluminum oxide

($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). The proposed name for this material is clachite.

Gibbsite and boehmite, the trihydrate and monohydrate, are soluble in a solution of sodium hydroxide at elevated temperature and pressure, whereas diaspore is practically insoluble. The solubility of these two minerals is the basis of the Bayer process of alumina extraction.

All bauxites contain certain impurities, the commonest of which, in the order of their importance, are: silica, principally as a constituent of kaolinite, and to a lesser extent as quartz; iron, as hematite, limonite, and siderite; and titanium, as ilmenite, rutile and leucoxene. Minor impurities are zircon, cobalt and nickel.

Bauxite is produced commercially in Arkansas, Alabama, Mississippi, Georgia and Tennessee, but the most important deposits in the United States are in Arkansas, in the vicinity of Little Rock.

HISTORY OF BAUXITE BENEFICIATION

The literature on bauxite beneficiation is limited, but the reports of Gandrud and DeVaney¹ and Clemmer, Clemmons, and Stacy² show the possibilities of flotation as a means of beneficiating bauxite. Their work has also developed reagent combinations that are satisfactory for flotation of gibbsite.

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¹ B. W. Gandrud and F. D. DeVaney: Bauxite Float-and-sink Fractionation and Flotation Experiments. Bur. Mines Bull. 212 (1929).

² J. B. Clemmer, B. H. Clemmons and R. H. Stacy: Preliminary Report on the Flotation of Bauxite. Bur. Mines R.I. 3586 (1941).

On a commercial scale, very little has been done in beneficiation other than washing. It is understood that considerable tonnages of South American bauxites have been treated in washing plants at the mines. In the United States some producers have tried washing and screening, but the products obtained from such operations have not been able to compete with high-grade bauxite.

SAMPLES TESTED

All of the tests reported in this paper were performed on samples from the Arkansas bauxite district in Saline and Pulaski Counties. The samples investigated were taken by the Bureau of Mines in the present program to prospect and delineate additional bauxite reserves. Most of the samples were obtained by core drilling, and the drill cores were composited in a manner to represent the largest tonnage existing in any deposit drilled.

METHODS OF BENEFICIATION

The silica in most Arkansas bauxite occurs as a constituent of kaolinite. In the majority of samples tested, the silica content can be materially reduced by flotation of the hydrous aluminum oxide, leaving the kaolinite in the tailing. The iron and titanium minerals, if not previously removed, are concentrated by flotation with the hydrous aluminum oxides. The general procedure that has been found to give the most satisfactory results in beneficiating bauxite consists of gravity or magnetic concentration for removal of the iron (ferric and ferrous) and titanium minerals, followed by flotation for the recovery of the hydrous aluminum oxides and rejection of the silica and other impurities. In some cases, it has been found desirable to use both gravity and magnetic concentration to remove the iron minerals because gravity concentra-

tion is not effective in removing very fine mineral particles.

Magnetic concentration has been found to be best suited to bauxite of low iron and titanium content. These minerals are only slightly magnetic, and a very intense field is required for their separation. The larger the quantity of iron and titanium in a material subjected to magnetic separation, the greater will be the loss of bauxite because of mechanical entrapment in the magnetic minerals.

FLOTATION REAGENTS AND CONDITIONS

The first prerequisite of satisfactory separation between the hydrous aluminum oxides and kaolinite in flotation is a dispersed pulp to avoid floccules of finely divided bauxite and clay. This may be accomplished on most bauxites by maintaining an alkaline pulp, but some may require additional dispersants. Sodium hydroxide is the preferred dispersant. Others, such as sodium carbonate and sodium sulphide, may be used, but are not as efficient in promoting flotation of the hydrous aluminum oxides. The list of dispersants that may be used is long, and the choice is optional.

The best results in the flotation of the hydrous aluminum oxides were obtainable in an alkaline pulp with a pH ranging from 8.7 to 10.0 during the first conditioning period and of approximately 8.6 in the final cleaning operation. Present tests indicate that a higher pH, or a more alkaline pulp, is required for separating the hydrous aluminum oxides from kaolinite as the proportion of kaolinite in the bauxitic material increases.

A two-stage conditioning period has been found to be most advantageous. The first stage is with the alkali and dispersant, if one is needed, and the other is with the collectors and frothers. Ample time should be given for all reactions to be completed in both stages. The

optimum time for each ore must be determined by trial.

A pulp consistency of 10 to 15 per cent solids gives the most satisfactory results, because a higher percentage of solids results in a pulp of high viscosity owing to the large amount of clay in most low-grade bauxite. A higher percentage of solids may be used, but it tends to lower the grade of the concentrate by the mechanical entrapment of a part of the dispersed clay in the pulp.

The most efficient collectors for the hydrous aluminum oxides are oleic acid and fish-liver-oil fatty acid, type C.* The fatty resinous by-products of the paper-mill waste liquor, such as Tallol,† Ligo‡ and Indusol,‡ are fairly effective as collectors of the hydrous aluminum oxides, but they are more pronounced frothers. When used in conjunction with oleic acid or fish-liver-oil fatty acid, type C, or in combinations of all three, they add materially to the quality of the froth and assist in the flotation of the hydrous aluminum oxide minerals.

Various metaphosphate, hexametaphosphate and pyrophosphate compounds have been used to "complex" and "tie up" the soluble salts of calcium, magnesium, iron, and aluminum, which tend to retard the flotation of gibbsite. These compounds are powerful dispersants and when used with sodium hydroxide materially aid in the flotation of the hydrous aluminum oxides in some bauxite, but in others tend to depress them.

Sodium hypochlorite has been found to be an effective activator of the hydrous aluminum oxides in some bauxites, but in others it has a depressing effect.

Hard water is detrimental to the flotation of the hydrous aluminum oxides,

probably because of the precipitation of the collectors as insoluble soaps.

In general, the consumption of reagents increases as the proportion of kaolinite to hydrous aluminum oxides increases.

METHOD OF ANALYSIS

The method of analysis used was the standard procedure for bauxite. The ferrous iron (FeO) was determined by a separate analysis. The silica (SiO₂), total iron (Fe₂O₃), titanium (TiO₂), and ignition loss were determined on another sample, and the alumina (Al₂O₃) was calculated by difference. This method does not differentiate between the hydrous aluminum oxides and the aluminum silicates.

The hydrous aluminum oxides that are recoverable by the Bayer process may be determined by a laboratory method that is patterned after it. The laboratory method is essentially the same as the commercial process and consists of dissolving the hydrous aluminum oxides in a solution of sodium hydroxide at high temperature and pressure. After filtration of the mixture, the aluminum hydroxide is precipitated from the solution by carbonation and filtered, washed, and ignited to form alumina.

In plant practice the alkali-soluble alumina has been found to be equivalent to the difference between the percentage of total alumina and 1.1 times the percentage of silica. In the laboratory determination this was also found to be true, especially on the low-silica bauxite. The calculation method of determining the available alumina was used in all cases, and frequent check analyses were made by the alkali-soluble method on various samples. The calculation method of determining the available alumina may be questioned, but at least it serves as a basis for comparing results.

RESULTS OF BENEFICIATION

From the numerous samples tested, the results on four bauxites were selected

* Product of the Arista Oil Products Co.

† Product of the Gulf States Paper Corporation.

‡ Products of the West Virginia Pulp and Paper Co.

to illustrate the various possibilities of concentration. These bauxites were typical of extensive deposits of high-silica material. The descriptions and analyses of these samples are given in Table 1.

Tests on all the bauxites except sample 1 were laboratory tests; a pilot-plant test was made on sample 1 and the results duplicated the results of laboratory testing. On this basis it may be assumed that the other samples could be treated with equal

SAMPLE 1. REICHARDT MINE, DULIN
BAUXITE COMPANY, PULASKI COUNTY

Concentration of Bauxite

The bauxitic material of sample 1 was of the oölitic type and contained about 18 per cent silica and 3 per cent iron. The bauxite mineral was gibbsite, and the principal gangue mineral was kaolinite. Amorphous bauxite was quite abundant and was intimately associated with the

TABLE 1.—*Analyses of Arkansas Bauxites Tested*
PER CENT

Sample No.	Property	Al ₂ O ₃		SiO ₂	Fe ₂ O ₃	TiO ₂	Ignition Loss
		Ttotal	Available ^a				
1	Reichardt mine, Dulin Bauxite Co., Pulaski County	50.7	30.7	18.2	2.9	3.2	25.6
2	Rummel, Treadway and Shackelford Properties, Pulaski County	45.7	24.8	19.0	7.2	2.6	23.6
3	B. A. Fletcher and Republic Mining Co. Properties, Saline County	42.8	11.8	28.2	5.5	1.8	20.5
4	L. L. Hempstead, Pulaski County	41.2	12.9	25.7	8.1 ^b	2.0	21.0

^a Calculated alumina available to the Bayer process.

^b Total iron as Fe₂O₃ was 8.1 whereas the ferrous iron as FeO was 6.1. The remainder of the iron calculated as Fe₂O₃ was 1.6.

efficiency in the pilot plant. A bauxite concentrate containing less than 8 per cent silica was recovered from each of the samples as shown in Tables 2, 5, 6 and 8. A tailing also was produced from each that would be a suitable product for treatment by the soda-lime sintering process to recover the remaining alumina. Titanium concentrates were produced from two bauxites, as shown in Tables 3 and 7, that might be usable in the manufacture of titanium pigments for the paint industry, and a low-grade zircon concentrate, shown in Table 7, was recovered that might be concentrated to a marketable grade. Concentration of another bauxite, shown in Table 4, demonstrated the possibility of recovering nickel and cobalt as by-products. The possibility of rejecting both ferrous and ferric iron is shown in Table 8.

kaolinite. In addition, there were minor amounts of ilmenite, siderite, quartz, cobalt-bearing and nickel-bearing minerals.

The ore was tested in the following manner in a pilot plant. The ore, stage-crushed to minus 6-mesh, was fed to a log washer, at the rate of 1 lb. per minute, for disintegration and removal of primary slimes before grinding. The log-washer overflow was classified in a bowl classifier. The combined sands of the log washer and bowl classifier were ground in a ball mill. The ball-mill discharge was tabled for the removal of the iron, titanium, nickel, and cobalt minerals and the table tailing was returned to the bowl classifier. The bowl-classifier overflow, essentially minus 100-mesh, was thickened to approximately 10 per cent solids. The thickened pulp was conditioned in two stages, first with sodium hydroxide and sodium hexa-

metaphosphate and then with oleic acid and Indusoil. The conditioned pulp was floated and the rougher concentrate cleaned four times. The middling from each successive cleaner was returned to the previous cleaner, and the middling from the first cleaner returned to the first conditioner for re-treatment.

Titanium Concentration

The high titanium content of the table concentrate, 26.3 per cent TiO_2 , indicated the possibility of further concentration to make a relatively high-grade ilmenite product. A composite sample of the table concentrates from several runs of the

TABLE 2.—*Bauxite Concentration, Pilot-plant Test on Sample 1*

Product	Weight, Per Cent	Analysis, Per Cent						Distribution, Per Cent			
		Al_2O_3		SiO_2	Fe_2O_3	TiO_2	Igni- tion Loss	Al_2O_3		SiO_2	Fe_2O_3
		Total	Avail- able					Total	Avail- able		
Table concentrate...	2.8	26.2	20.9	4.8	25.9	26.3	11.4	1.4	1.8	0.7	24.5
Flotation concentrate	40.2	56.0	48.4	6.9	2.9	3.7	30.7	43.6	59.9	15.9	39.3
Tailing.....	57.0	49.8	21.8	25.5	1.9	2.0	21.2	55.0	38.3	83.4	36.2
Composite (head)....	100.0	51.6	32.4	17.5	3.0	3.4	24.7	100.0	100.0	100.0	100.0

Reagent	Pounds per Ton of Feed			
	Conditioner 1	Conditioner 2	Rougher	Cleaners 1 to 4
Sodium hydroxide.....	3.3			
Sodium hexametaphosphate.....	0.7			
Oleic acid.....		3.3		
Indusoil.....		0.5		
pH.....	8.7	8.5		
Per cent solids.....	10	10	8.5	8.5
Time, minutes.....	5	5	10	5-3
				5-2

TABLE 3.—*Ilmenite Concentration by Tabling of Table Concentrate from Sample 1*

Product	Weight, Per Cent	Analysis, Per Cent				Distribution, Per Cent			
		TiO_2	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	Al_2O_3	SiO_2
Concentrate.....	13.3	39.7	39.2	7.9	2.0	40.1	35.0	2.8	2.7
Middling.....	10.9	27.7	33.2	13.2	5.0	23.0	24.3	3.9	5.6
Tailing.....	75.8	6.4	8.0	45.4	11.9	37.9	40.7	93.3	91.7
Composite (feed).....	100.0	13.2	14.9	36.9	9.8	100.0	100.0	100.0	100.0

The results of the bauxite concentration are shown in Table 2.

The high loss of available alumina in the tailing (38.3 per cent) was caused by the hydrous aluminum oxides, which could not be floated when extremely fine in size and intimately associated with kaolinite.

pilot plant was crushed to minus 20-mesh. The minus 20-mesh material was classified into three sand products and a slime product, each of which was retailed, making three products—concentrate, middling, and tailing. The results of the titanium concentration are shown in Table 3. No attempt was made to improve

the recovery or grade of the ilmenite concentrate, but the information is presented to show the possibility of a by-product that may be obtained from this ore.

Nickel-cobalt Concentration

Microscopic examination of the pilot-plant table concentrate indicated the presence of nickel and cobalt, and a study was made to determine their amenability to concentration.

The analysis of the table concentrate was 0.08 per cent nickel; 0.05 per cent cobalt.

A sample of the original table concentrate was crushed through 20-mesh and ground in stages to minus 100-mesh for flotation. The pulp was conditioned and floated, and the rougher concentrate cleaned twice.

The results of the cobalt-nickel concentration are shown in Table 4. As the

TABLE 4.—*Flotation of Nickel and Cobalt of Table Concentrate from Sample 1*

Product	Weight, Per Cent	Analysis, Per Cent		Distribution, Per Cent*	
		Nickel	Cobalt	Nickel	Cobalt
Concentrate...	0.7	4.93	2.29	45.8	31.4
Middling 2...	1.9	0.17	0.19	4.2	7.1
Middling 1...	10.1	0.12	0.05	15.8	10.0
Tailing.....	87.3	0.03	0.03	34.2	51.5
Composite (feed).....	100.0	0.08	0.05	100.0	100.0

Operating Data

Reagents	Pounds per Ton of Feed			
	Conditioner	Rougher	Cleaner 1	Cleaner 2
Lime.....	0.5			
R-208 ^b	0.03			
R-301 ^b	0.03			
Sodium Aerofloat ^b ...	0.03			
Sodium sulphide...	0.02			
Pine oil GNS No. 5	0.08			
pH.....	7.7	7.7	7.9	8.0
Time, minutes.....	3	3	2	2

* Percentage of the total in the table concentrate.

^b American Cyanamid Co., New York.

nickel and cobalt in the original ore were so low that an analysis could not be made, it is not possible to calculate the over-all recoveries.

SAMPLE 2. RUMMEL, TREADWAY AND SHACKELFORD PROPERTIES, PULASKI COUNTY

Bauxite Concentration

Sample 2 was mainly gibbsite, amorphous bauxite, and kaolinite, with smaller amounts of siderite, iron oxides, and ilmenite. Very small quantities of quartz, mica, and carbonaceous material were also present. The iron oxide was present as limonite and hematite, probably as oxidation products of the siderite, and was intimately associated with amorphous bauxite.

The sample was crushed to minus 20-mesh and deslimed. The granular product was tailed to remove iron and titanium minerals. The table tailing and slime were combined and ground to minus 100-mesh for flotation. The ground pulp was conditioned in two stages and floated. The rougher concentrate was cleaned three times. Water softened with Zeolite was used in both grinding and flotation.

The results of the concentration of this sample are shown in Table 5. The grade of the bauxite produced from sample 2 could be increased if desirable by the use of magnetic separation for removal of additional iron minerals before flotation.

SAMPLE 3. B. A. FLETCHER AND REPUBLIC MINING COMPANY PROPERTIES, SALINE COUNTY

Concentration of Bauxite

Sample 3 was composed principally of kaolinite, gibbsite, and amorphous bauxite, with some siderite, manganosiderite, hematite, and limonite. Ilmenite and quartz were present in small amounts, and very small amounts of zircon, mica, leucocene,

TABLE 5.—*Bauxite Concentration, Table Concentration and Flotation of Sample 2*

Product	Wt., Per Cent	Analysis, Per Cent							Distribution, Per Cent			
		Al ₂ O ₃		SiO ₂	Fe ₂ O ₃ ^a	FeO	TiO ₂	Igni- tion Loss	Al ₂ O ₃		SiO ₂	Fe ₂ O ₃
		Total	Avail- able						Total	Avail- able		
Table concentrate..	8.9	14.8	8.2	6.0	46.0	39.6	3.5	27.0	2.9	2.9	2.9	52.2
Bauxite concentrate	45.7	52.2	44.1	7.4	7.4	5.1	3.3	29.5	52.8	81.2	18.3	37.2
Middling 3.....	5.0	45.9	15.0	28.1	2.3	1.1	2.2	21.0	5.1	3.0	7.6	1.5
Middling 2.....	7.7	45.3	12.2	30.1	1.9	0.6	2.1	20.0	7.7	3.8	12.5	1.9
Middling 1.....	10.8	44.1	9.0	31.9	1.9	0.6	2.1	19.6	10.6	3.9	18.6	2.7
Tailing.....	21.9	43.2	5.9	33.9	1.6	0.5	1.8	18.6	20.9	5.2	40.1	5.5
Composite (head) ..	100.0	45.2	24.8	18.5	7.8	6.1	2.7	24.6	100.0	100.0	100.0	100.0

Operating Data

Reagents	Pounds per Ton of Feed					
	Conditioner 1	Conditioner 2	Rougher	Cleaner 1	Cleaner 2	Cleaner 3
Sodium hydroxide.....	2.0					
Sodium hypochlorite.....	0.5					
Fish-liver-oil fatty acid, type C.....			2.0			
American Cyanamid reagent 708 ^b			1.0			
pH.....	9.5		9.3	8.8	8.7	
Per cent solids....	15	15	15	10	9	8
Time, minutes.....	5	5	10	5	5	4

^a Total iron as Fe₂O₃.^b Fatty acid of vegetable origin.TABLE 6.—*Table and Magnetic Concentration and Flotation of Sample 3*
CONCENTRATION OF BAUXITE AND HIGH-ALUMINUM CLAY

Product	Wt., Per Cent	Analysis, Per Cent							Distribution, Per Cent			
		Al ₂ O ₃		SiO ₂	Fe ₂ O ₃	TiO ₂	Igni- tion Loss		Al ₂ O ₃		SiO ₂	Fe ₂ O ₃
		Total	Avail- able						Total	Avail- able		
Table concentrate...	10.8	24.6		28.4	19.9	5.6	18.4		6.1		11.1	43.3
Magnetic concentrate	1.6	18.1	8.8	8.5	41.3	5.5	23.8		0.7	1.0	0.5	13.3
Bauxite concentrate..	21.5	56.7	48.3	7.6	3.7	1.9	28.9		27.7	73.3	5.9	16.1
Middling 3.....	3.0	48.4	21.9	24.1	2.5	1.7	21.8		3.3	4.7	2.6	1.6
Middling 2.....	7.1	45.9	14.7	28.4	2.5	1.5	20.4		7.4	7.3	7.3	3.6
Middling 1.....	17.2	45.2	10.4	31.6	2.1	1.2	19.0		17.7	12.6	19.6	7.2
Tailing.....	38.8	42.1	0.4	37.9	1.9	1.1	17.2		37.1	1.1	53.0	14.9
Composite (feed)	100.0	44.0	13.4	27.7	5.0	1.9	20.6		100.0	100.0	100.0	100.0

Operating Data

Reagents	Pounds per Ton of Feed					
	Conditioner 1	Conditioner 2	Rougher	Cleaner 1	Cleaner 2	Cleaner 3
Sodium hydroxide.....	3.0					
Sodium hypochlorite.....	0.5					
Oleic acid.....			0.8			
Fish-liver-oil fatty acid, type C.....			1.0			
American Cyanamid reagent 708.....			1.0			
pH.....	10.0		9.9	9.9	9.0	8.7
Time, minutes.....	5	5	10	6	5	3
Per cent solids....	14.0	14.0	14.0	7.5	6.0	4.0

and carbonaceous material were also present.

The following procedure was used in testing: A portion of the sample was ground to minus 20-mesh and hydraulically classified into two granular products and a slime. The granular products were tabled separately for removal of the iron and titanium minerals. Similar products were combined, and the table tailing was combined with the slime. The combined table tailing and slime was ground to minus 100-mesh and the ground pulp passed through a high-intensity magnetic separator for removal of additional iron and titanium minerals not already removed by table concentration. The non-magnetic tailing was then thickened, conditioned in two stages, and floated. The rougher concentrate was cleaned three times. Zeolite-softened water was used in both grinding and flotation. The results of the test are given in Table 6.

Ilmenite and Zircon Concentration

Examination of the table concentrate from testing sample 3 indicated the presence of considerable ilmenite and zircon, therefore an attempt was made to concentrate these minerals. The original table concentrate was retabled without further grinding or sizing, and a product was recovered that contained 20.0 per cent titanium oxide and 6.3 per cent zirconium oxide. The results of the titanium-zircon concentration are shown in Table 7.

No attempt was made to separate the two minerals or increase the grade. Micro-

scopic examination showed that both minerals were free, and careful sizing followed by gravity concentration and magnetic separation would undoubtedly produce high-grade products.

SAMPLE 4. L. L. HEMPSTEAD PROPERTY, PULASKI COUNTY

Bauxite Concentration and Rejection of Ferrous and Ferric Iron

Sample 4 was composed mainly of kaolinite, gibbsite and amorphous bauxite, with smaller amounts of siderite, iron oxides and ilmenite. Very small quantities of quartz, mica and carbonaceous materials were also present. The iron oxides were present as hematite and limonite and were intimately associated with amorphous bauxite and kaolinite.

The sample was crushed to minus 20-mesh and deslimed in a hydraulic classifier. The granular product was tabled for removal of the iron and titanium minerals. The table tailing was combined with the slime, and a portion of this material was ground to minus 100-mesh. The ground pulp was passed through a Frantz Ferrofilter, for removal of additional iron and titanium minerals. The non-magnetic tailing was then conditioned in two stages for flotation. The conditioned pulp was floated, and the rougher concentrate was cleaned three times without additional reagents. Zeolite-softened water was used in both grinding and flotation.

The results of the concentration of bauxite and rejection of ferrous iron are shown in Table 8.

TABLE 7.—*Titanium and Zircon Concentration*

Product	Weight, Per Cent	Analysis, Per Cent					Distribution, Per Cent				
		TiO ₂	ZrO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	ZrO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂
Concentrate.....	5.4	20.0	6.3	32.8	18.3	8.4	19.2	26.4	8.9	4.0	1.6
Tailing.....	94.6	4.8	1.0	19.1	25.0	29.6	80.8	73.6	91.1	96.0	98.4
Composite (feed)...	100.0	5.6	1.3	19.9	24.6	28.4	100.0	100.0	100.0	100.0	100.0

TABLE 8.—*Table Concentration, Magnetic Separation, and Flotation of Sample 4*
CONCENTRATION OF BAUXITE AND REJECTION OF IRON

Product	Wt., Per Cent	Analysis, Per Cent						Distribution, Per Cent				
		Al ₂ O ₃		SiO ₂	Fe ₂ O ₃	FeO	Igni- tion Loss	Al ₂ O ₃		SiO ₂	Fe ₂ O ₃	FeO
		Total	Avail- able					Total	Avail- able			
Table concentrate..	8.6	16.4	7.3	8.3	3.2	36.1	26.8	3.4	4.5	2.9	17.2	50.9
Magnetic concen- trate.....	4.8	24.2	17.9	5.7	5.1	27.6	27.4	2.8	6.1	1.1	14.7	21.7
Composite (table and magnetic concen- trate).....	13.4	19.2	11.1	7.3	3.9	33.0	27.0	6.2	10.6	4.0	31.9	72.6
Cleaner concentrate	15.1	53.8	46.7	6.5	0.9	4.3	28.4	19.4	49.9	3.9	8.6	10.7
Middling 3.....	2.7	44.9	16.7	25.6	1.8	2.9	20.8	2.9	3.2	2.7	3.1	1.3
Middling 2.....	8.0	44.1	12.8	28.5	1.4	2.4	19.6	8.4	7.2	9.0	6.7	3.1
Middling 1.....	19.9	43.0	6.8	32.9	1.2	1.5	18.0	20.5	9.5	26.0	14.7	4.9
Tailing.....	40.9	43.6	6.8	33.5	1.4	1.1	17.4	42.6	19.6	54.4	35.0	7.4
Composite (head)...	100.0	41.8	14.1	25.2	1.6	6.1	20.7	100.0	100.0	100.0	100.0	100.0

Operating Data						
Reagents	Pounds per Ton of Feed					
	Conditioner 1	Conditioner 2	Rougher	Cleaner 1	Cleaner 2	Cleaner 3
Sodium hydroxide.....	3.0					
Sodium hypochlorite.....	0.5					
Sodium hexametaphosphate.....	0.25					
Fish-liver-oil fatty acid, type C.....		1.5				
American Cyanamid reagent 708.....		1.0				
pH.....	9.9	9.7	9.7	9.4	9.0	8.6
Per cent solids.....	13.5	13.5	13.5	7.0	5.0	4.5
Time, minutes.....	5	5	7	4	4	2.5

DISCUSSION OF RESULTS

The samples selected for beneficiation were representative of fairly extensive deposits of high-silica bauxite.

Products containing less than 8 per cent silica were produced from all samples by ore-dressing methods, and the tailing products would be suitable for treatment by the soda-lime sinter process of alumina extraction. The results have been confirmed by duplicate tests on numerous samples of similar high-silica bauxite.

By-products from two of the samples were indicated. Each bauxite ore, however, would have to be individually studied to determine the type and kind of by-product, if any, that could be made.

The commercial flowsheet for beneficiation of high-silica bauxite would necessarily have to be very flexible to accommodate

the rapid change of the grade and character of the material, especially in the removal of the iron and titanium minerals.

Separation of the hydrous aluminum oxides from kaolinite by flotation can be accomplished on most bauxitic materials, except when a large quantity of hydrous aluminum oxides occurs in the amorphous state and is intimately associated with kaolinite.

The reagent combinations used were considerably different for the four samples; however, other tests not reported indicated that any combination of the two collectors, oleic acid and fish liver oil, gave equally good results. The use of the frothers, Indusoil and American Cyanamid reagent 708, was a matter of choice. Sodium hexametaphosphate and sodium hypochlorite as used in the additional tests were found to be optional, and their omission had little effect on the final results.

Alumina from Clay by the Lime-sinter Method

By F. R. ARCHIBALD* AND C. F. JACKSON,† MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE prospect of winning aluminum from clay was recorded almost a century ago at a time when the metal was no more than a curiosity.‡ As the industry developed, and it has probably developed faster than that of any other metal, the expanding need for raw materials was adequately met by the ample supplies of bauxite ore. As with the other metals older in industry, however, lower grade ores have gradually entered the raw-material field through improvements in ore dressing, insufficiency of high-grade ore supplies, favorable geographic location, or national necessity for domestic supply. So with aluminum, or alumina, which has been established as the requisite intermediate, the time may have come when a satisfactory process, with favorable location and suitable raw materials, can hold a sound place both in metallurgy and economics. It is the purpose of this paper to describe the Ancor process and its proposed application in treatment of clay in a plant now under construction at Harleyville, South Carolina, by the Defense Plant Corporation.

DEVELOPMENT OF THE ANCOR PROCESS

The Ancor process has developed through successive stages of laboratory investigation, pilot-plant demonstration using nepheline syenite and pilot-plant demonstration using kaolin-type clay from South Carolina, and is now in preparation for unit trial on an operating plant basis using the latter material.

The laboratory studies were carried out over a number of years in the laboratory of the American Nepheline Corporation in Rochester, N. Y., and for the same company in the ore-dressing laboratory of Beattie Gold Mines, Que. Ltd. at Duparquet, Quebec. Both companies are associated with Ventures Ltd., Toronto, and its associated American companies. The work was originally undertaken with a view to recovery of alumina and alkalis from nepheline syenite as an adjunct to the American Nepheline Company's established business in the glass and ceramic trades, but as a process developed the possibility of application to clay and other aluminous raw materials became apparent and the laboratory studies were broadened to include these as well.

Under the more pressing impetus of wartime needs and possibilities, pilot-plant operations were undertaken at the Canadian Bureau of Mines Ore Dressing Laboratories in Ottawa, and for purposes of demonstration under joint sponsorship of the Canadian Bureau of Mines, The American Nepheline Corporation, and The Aluminum Company of Canada Ltd. Upon completion of this program, of

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‡ Moreover, when we know that aluminum exists in considerable proportion in clays, and that this proportion may amount to as much as one fourth of their weight in certain of the commonest materials, we naturally wish that sooner or later aluminum may be introduced into industry. (H. Sainte-Claire Deville: *De l'aluminium*; 1855 and 1859.)

which the results were considered to be sufficiently satisfactory, the pilot-plant work on nepheline syenite and association of these sponsors was terminated. The results had been sufficiently satisfactory to warrant exploration by Ventures Ltd. and their American associates, Panaminas Incorporated and American Nepheline Corporation, of deposits of suitable aluminous materials in several localities in the United States and Canada with a view to exploitation of the most favorably located and largest reserves.

One of the favorable localities where extensive deposits of high-grade materials were proved to exist developed in the state of South Carolina. The results of the entire investigation to date were laid before the War Production Board and War Metallurgy Committee and, being favorably received, steps were taken to resume pilot-plant operations using the clay and limestone raw materials available in the specific area selected as most favorable. Following satisfactory demonstration of the main operations required in the process, and submission of field data indicating adequate reserves, a proposal embodying use of the process in the selected locality was accepted as part of the program set up by the War Production Board toward assurance of adequate alumina supply.

This acceptance was followed by the award by Defense Plant Corporation of a contract for the erection of a plant, to Ancor Corporation, which had been formed earlier by Panaminas Incorporated and American Nepheline Corporation for the purpose of furthering the application of the process on a commercial scale.

GENERAL CONSIDERATION OF ALUMINA PROCESSES

A comprehensive review of processes proposed or tried up to the year 1930 for winning of alumina from a variety of

raw materials was given by Edwards, Frary and Jeffries.¹ Since that time a number of papers have appeared in the technical and patent literature but it is not considered within the scope of the present paper to review this literature at length. Reference is made however to a series of Russian articles dealing with extensive studies in recovery of alumina from two types of materials, those containing alkalis, alumina and silica, such as nepheline syenite,² and those containing no alkali, such as kaolin.³

The Russian references are cited in particular because they are quite detailed, describe a process on which sizable pilot-plant operations were conducted and which are reported to have been projected to full-scale production in the Volhov Aluminum Works. They appeared, moreover, at a time when the Ancor process was under development and in some measure paralleled this development.

In general, the more recent alkaline processes for extraction of alumina from highly siliceous raw materials make use of calcium oxide for fixation of the silica and fall into two classes with reference to the device for fixation of the alumina. In one group soda is added to the raw-material mix for the latter purpose, and in the other a further addition of lime is made for that purpose, the two types being designated as soda-lime-sinter and lime-sinter processes, respectively. The Ancor process, as applied to clay, is purely of the latter classification; as applied to raw materials such as nepheline syenite, which naturally contain alkalis in combination, the designation is not entirely distinct.

Designation of a process as soda-lime-sinter or lime-sinter, referring as it does only to the raw-material mixture used, is merely a general classification. A complete process involves several steps, in

¹ References are at the end of the paper.

any of which special devices or treatment may distinguish one process from another. Broadly, the requisite steps are: (1) preparation and mixing of raw materials;

of the Ancor process are illustrated in the flow diagram (Fig. 1).

In implementing this flowsheet into plans for a plant to produce 50 tons of

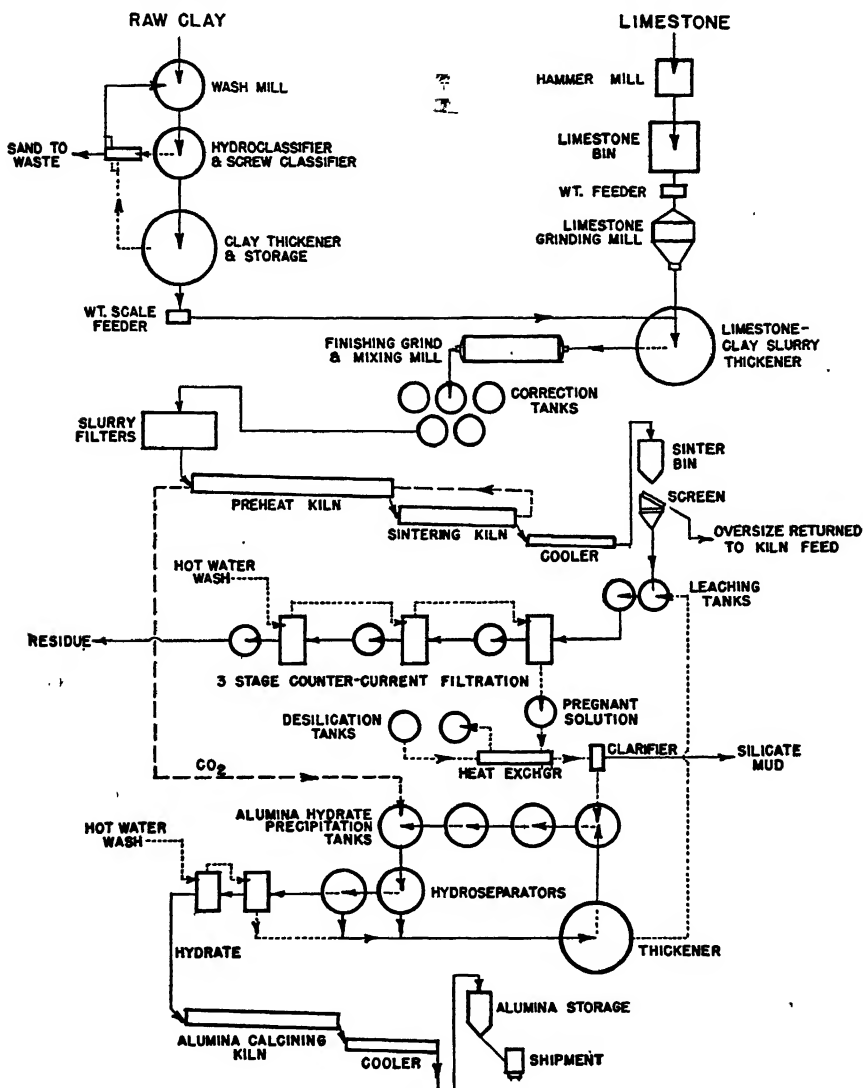


FIG. 1.—FLOWSHEET OF ANCOR PROCESS.

(2) furnacing; (3) leaching; (4) purification of solution; (5) recovery of alumina trihydrate from solution; and (6) calcination of the hydrate to oxide. The sequence and interrelationship of these steps as part

calcined alumina per day, there has been adherence as far as possible to the following guiding principles: (1) continual reference to and interpretation of laboratory and pilot-plant results and behavior of mate-

rials; (2) simplicity; (3) continuous rather than batch operations; and (4) use of devices and procedures developed in and peculiar to the Ancor process.

TECHNICAL DISCUSSION

In consideration of any alkaline process for recovery of alumina, it should be realized that all such processes must have features in common. Moreover, in technical research generally, information available from the work of others must have a bearing on the course of an investigation, and therefore on the details of any process developed. These two observations are made as a general statement of background and in caution to the reader, who may see the process illustrated in the flow-sheet as a modification of one or another with which he may be familiar. In pursuing the present investigation beyond the preliminary stage, difficulties were met with, in the solution of which it is considered that a distinct process has been established.

From the rather voluminous literature can be gleaned early references with respect to the broad principles of proportioning siliceous ores of alumina with lime to fix the silica as dicalcium silicate and additional lime to form calcium aluminates as well as leaching with sodium carbonate solutions, desilication of aluminate solutions by treatment at elevated temperatures, and precipitation of alumina trihydrate by the use of carbon dioxide. Since these have been well summarized, with references, by Edwards, Frary and Jeffries,¹ the reader is referred to their work.

Question frequently has been raised as to extraction possible by the lime-sinter method followed by soda leaching. In answer it can be stated that in the course of the investigation herein described extraction of 96 per cent of the alumina content has been made from clay, using precipitated calcium carbonate as the

source of lime and 91 per cent using high-grade limestone. Other investigators have recently reported 97 per cent extraction from a clay sample furnished by Ancor Corporation, using precipitated calcium carbonate.⁴ In view of these results it appears that primary extraction in an operating plant will be limited only by the purity of raw materials, the adequacy of mechanical engineering and soundness of ore-dressing technique. The relationship of various factors encountered in the several process steps are dealt with in the following description and discussion.

Preparation of Raw Materials

Since each pound of silica in the raw materials requires limestone equivalent to 3.3 lb. of pure CaCO_3 , it is important economically to remove as much free silica from the clay as possible before mixing. A conventional clay-washing arrangement is shown in Fig. 1, which, as well as eliminating sand, furnishes several days storage of uniform clay feed.

The limestone found in the area selected for this project is of loose texture and requires little crushing and primary grinding. The order of arrangement of the equipment shown in the preparation section is based on laboratory test results and is designed to yield maximum pulp density and uniformity of composition in the filter feed.

Actual results of analysis of one shipment of raw materials used in pilot-plant operations (dry basis) are shown in Table 1.

TABLE 1.—*Analysis of One Shipment of Raw Materials Used in Pilot Plant*

Constituent	Limestone	White Clay	Red Clay
SiO_2	1.42	44.60	45.04
Al_2O_3	0.52	39.70	38.40
$\text{Fe}_2\text{O}_3 + \text{TiO}_2$	0.68	1.84	4.38
P_2O_5	0.08		
CaO	53.30	0.12	0.07
MgO	1.08	0.06	0.06
SO_3	0.36		
Ignition loss.....	42.49	13.71	11.66

In actual operations it is anticipated that in avoiding the necessity for selective mining the raw clay will contain silica (as sand) in excess of that shown, and a proportion of red clay. The sand content will be taken care of in the manner illustrated; the iron and titania content, if of the order shown, is neglected in calculating the mixture. For purpose of illustration, this calculation for white clay is as follows:

100 lb. limestone contain 1.42 lb. SiO_2 and
0.52 lb. Al_2O_3

Requirement for 2 (CaO)·SiO₂ equals 2.64 lb.
CaO

Requirement for 1.5 (CaO)·Al₂O₃ equals 0.43
lb. CaO

Total inactivated CaO content of limestone equals 3.07 pounds

Net available CaO content of limestone
50.23 per cent (I)

100 lb. white clay contain 44.6 lb. SiO_2 and 39.7 lb. Al_2O_3

Requirement for 2 (CaO)·SiO₂
equals 83.2 lb. CaO

Requirement for 1.5 (CaO)·Al₂O₃
equals 32.7 lb. CaO

Total CaO requirement
115.0 pounds (2)

From results 1 and 2:
Total limestone required for 100 lb. clay

Ratio of limestone to clay equals 2.31

In consideration of minor constituents in raw materials, those of chief concern are magnesia, iron oxide and titania. It developed during the work on nepheline syenite that magnesian limestones were not suitable in the process and that nepheline syenites containing high ferromagnesian mineral content required special treatment. Others⁵ have recently shown that even small amounts of magnesia may be harmful. Small percentages of iron and titania (less than 3 per cent in sinter) do not appear to be serious, and, in fact, the slight fluxing action caused by their presence is considered an advantage. Respecting fineness of grind required in preparation of the raw materials, it can be said that grinding of the final mixture to 90 per cent minus 200-mesh is desirable. Whether this fine or finer grinding develops in operation will be determined by the

balance of excessive costs of extremely fine grinding against the diminishing increase in extraction of alumina.

Sintering

A rotary kiln fired concurrently with the feed is considered the most satisfactory type of furnace. The temperature required is 2400° to 2500°F., influenced by the amount of iron and other fluxing constituents; and the time of contact may be one hour or less. Preheating may extend this time profitably, but not necessarily as far as reactions are concerned. Sinter that decrepitates (owing to dicalcium silicate inversion, beta to gamma form) to completeness after discharge from the kiln gives the best alumina extraction and is the most easily handled in leaching. Material that does not dust down on cooling may profitably be returned to the kiln as a circulating load. It has been shown that such material will decrepitate after a second pass through the kiln. In the pilot-plant operation it has been found possible to produce sinter containing less than 5 per cent undecrepiated material. In an operation on a larger scale, it probably could be almost entirely eliminated. The sinter, after cooling and completion of decrepitation, is screened through a 65-mesh screen to separate improperly burned material.

Leaching

The kiln product after dusting to a fine powder shows excellent physical behavior in leaching and filtering, provided the operation is kept within limits as to time, temperature and concentration of solution. The most satisfactory leaching procedure, yielding 83 per cent extraction of alumina from pilot-plant sinter, involved leaching 20 min. at 158°F.; use of a 2:1 mol ratio of Na_2O to Al_2O_3 and a concentration equivalent to 85 grams Al_2O_3 per liter of solution.

More recent work on laboratory sinters indicates that as good extraction of alumina, with less dissolution of silica and more economical operation, can be made at lower temperatures (145°F.). When the possibilities for variation and complexity are considered, with respect to sinter composition, through comparatively small changes in composition of raw materials and their mixtures, it will be realized that definition of optimum leaching conditions on sinter produced in a laboratory muffle may not agree with those found for sinter produced in a rotary kiln.

Necessity for other variations may result from treatment of clays of different composition or use of limestones from different sources. The variations necessary in procedure are no doubt reflections of variations in relative amounts of the calcium aluminate phases present, and of phases due to magnesia, iron and titania content. It is expected that in operation a set of conditions will evolve suited to the raw material used, manner of furnacing, and balance with the succeeding operations. A parallel might be drawn with many smelting, leaching and other metallurgical operations in which operating conditions must be changed to suit changes in ore composition or earlier process steps such as flotation or roasting.

It is the main object of leaching to make maximum alumina extraction. It is highly desirable as well in operation of the present process to have maximum concentration of pregnant solution, minimum volume of wash water, and minimum dissolution of silica in accordance with the main object. It is desirable to have maximum concentration so that size of equipment, particularly desilication equipment, may be kept as small as possible and that heat requirements may be kept low. It is essential that wash water be kept within the limits of incidental evaporation in the kilns and tanks and elimination in a wet residue. It will be noted that no evaporators are

included in the flowsheet. It is desirable to keep the silica content of pregnant solutions as low as possible, since a proportionate amount of alumina is thrown out of the solution with it during pressure treatment. Although this contained alumina need not be physically lost (it is returned to the circuit), the economy of a circulating load is frequently poor. The silica dissolved is ordinarily from 1.5 to 3 per cent of the alumina extracted.

Desilication

In all alkaline processes for extraction of alumina from ores, the most troublesome impurity is silica. From experience, it appears that, unless special means are adopted, extraction of better than 80 per cent of the alumina content of a sinter is accompanied by silica dissolution equivalent to at least 2.5 per cent of the alumina plus silica content of the solution. Reduction of this amount of dissolved silica may be sought in several ways, including:

1. Attention to the composition of the raw mixture of clay and limestone. Increasing the proportion of lime tends to reduce the amount of silica dissolved in leaching but worth while reduction necessitates uneconomical increase in limestone used and results in lowered alumina extraction.

2. Attention to furnacing details, particularly temperature, time of contact, and kiln atmosphere. In this respect too, improvements toward insolubility of silicate compounds tend toward lessened solubility of alumina as well.

3. Adoption of special leaching procedures, which may either tend to prevent the dissolution of silica or reprecipitate it into the residue during leaching. Among devices of this sort are those due to Pederesen⁶ and Martin.⁷

4. Treatment of the solution in a separate process step after leaching and filtering, with the object of precipitating the silica. Various modifications described in

the literature have been summarized by Edwards, Frary and Jeffries (pp. 159 and 160 of ref. 1).

In application of the Ancor process the last mentioned type of procedure receives most attention, although provision is also made in the countercurrent leaching arrangement, so that any advantage that may be gained by the use of partially saturated aluminate solutions⁷ for the first contact is provided for.

Early in the studies upon which this process is based it was noted that the most obvious means of removing silica from aluminate solutions would seem to be duplication of the mechanism of the Bayer digestion as far as the variables relevant to solubility of alumina and insolubility of silica were concerned. Bayer had noted in his patent specification that under the conditions of the digestion he proposed for bauxite some alumina, with soda and silicic acid, formed "the well-known double salt Na_2O , Al_2O_3 , 3SiO_2 , Aq. "⁸

A fundamental difference between treating bauxite by the Bayer process and lime sinter by the present process is that in the former all of the silica, if possible, is rendered insoluble as a sodium aluminum silicate; and in the latter most of the silica has already been inactivated with lime. It would not be sensible to reverse this gain during the leaching step, at the expense of soda and alumina loss. It seemed preferable to use a leaching procedure that gave the highest possible alumina extraction and to reduce the silica content by a subsequent and separate treatment of the solution.

In simple terms, the desilication treatment consists of a repetition of the conditions existing during a Bayer digestion in which silica is converted to an insoluble compound or compounds. Lack of solids that might serve as collectors or crystal growth centers may be made up by addition of fine solids such as clay. Colloidal agents such as starch or chemical agents such as

lime or magnesia are useful in speeding or completing the desilication.

Precipitation and Calcining of Alumina

After desilication treatment and clarification in a pressure filter, the pregnant aluminate solution is allowed to cool somewhat, a seed-charge of fine hydrate is added and the alumina is brought out of solution by a combination of seeding and carbonation.

By the same procedure, the soda in solution is reconverted to carbonate suitable for return to the leaching step. The classification, filtering and calcination of alumina hydrates has been adequately described by other writers and as no novel features are introduced in the Ancor process the subject is not enlarged upon here.

ECONOMIC FACTORS

Laboratory research and pilot-plant operation have demonstrated that alumina of high purity can be produced by the Ancor process from a considerable variety of aluminous raw materials, including various clays, nepheline syenite, anorthosite, spodumene, red mud and high-silica bauxite.

The cost of producing alumina from such materials will vary between wide limits, depending upon a number of factors. Some of these are technical and their effect on costs is apparent from the foregoing discussion of the process. Other factors, however, may have equal or greater effect upon production cost, as discussed briefly below.

In general, it may be stated that the requirements for economic application of the Ancor process are: large reserves of aluminous raw materials or ore and of high-calcium limestone that can be mined and brought together at the plant at low cost; thus the ore and limestone must be situated close together geographically. These requirements are met in relatively few of the

many localities in the United States and Canada that were investigated and considered by Ancor as desirable locations for a commercial plant.

content to warrant exploitation by the Ancor process are much more limited. Of the areas where these materials are known to occur and to contain enough

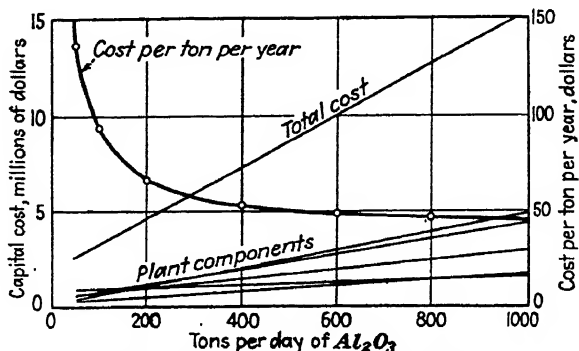


FIG. 2.—PLANT COST PER TON OF CAPACITY.

Capital Requirements

The plant-installation cost per ton of annual alumina capacity varies between wide limits, depending largely upon the size of the plant. Thus, for a small plant for production of 100,000 lb. (50 tons) of calcined alumina per day, the installation cost will be from \$130 to \$150 per ton of annual capacity, whereas for a plant to produce 2,000,000 lb. (1000 tons) per day, this cost would be reduced to \$45 to \$50 per ton. (See Fig. 2, based on engineering estimates for a specific area where the ore is clay.)

At the lower rate of production the amortization charge against production cost would be too high for an attractive commercial operation, whereas amortization charges for plants having a capacity of 500 tons or more daily would be reasonable.

Since small plants could not be expected to pay out on the investment in a reasonable term of years, a successful commercial plant must be a fairly large one. This in turn requires that large reserves of raw materials be available.

Although large deposits of aluminous raw materials occur throughout the United States, those of high enough alumina

alumina for consideration, only a few have been adequately explored to determine that the reserve tonnage is indeed ample to warrant construction of a plant of large capacity. The field is narrowed further by the requirement that limestone deposits of high purity be within economical shipping distance of the ore deposits.

Raw Materials

It is obvious that, other factors being the same, production costs will be lower the higher the alumina content of the ore and the higher the net available CaO content of the limestone.

Of the raw materials investigated (with the exception of bauxite and bauxitic clays), the kaolin clays contain the highest percentage of Al_2O_3 . Based on estimates of production costs, the authors became convinced that if no allowance is made for by-products, kaolin clay is the most economical ore for production of alumina by the Ancor process. For the past year the Ancor investigation in the laboratory and pilot plant have been confined principally to the use of clay, and exploration work to the development of reserves of high-alumina clay.

The lowest grade of clay (lowest in Al_2O_3 content) that could be utilized commercially has not been established, and would vary with mining costs, freight

of the clay decreases and the SiO_2 content increases. Although broadly the SiO_2 increases as the Al_2O_3 decreases, the relationship is not constant in natural

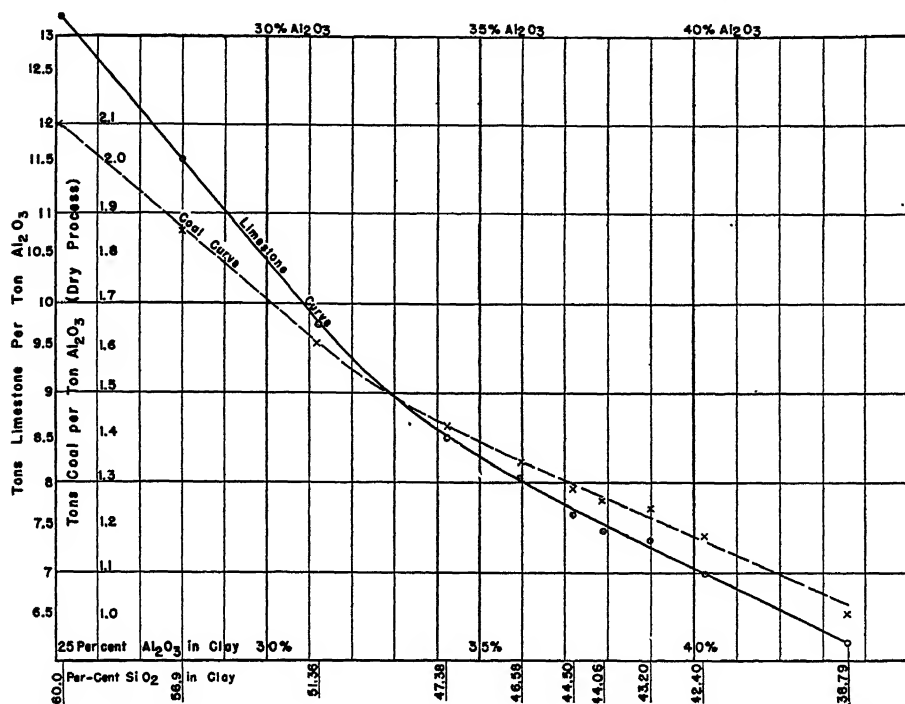


FIG. 3.—RELATION TONS LIMESTONE (50 PER CENT NET CaO) PER TON ALUMINA FOR ANCOR PROCESS, ALUMINA AND SILICA IN CLAY VARIABLE.

and power rates, fuel costs, and other factors, as well as the amenability of the clay to beneficiation and the cost thereof. For the present, however, Ancor has confined its attention to clays averaging 35 per cent Al_2O_3 or better.

Actual exploration has been confined to four localities selected from over 60 areas in 14 states where investigations have revealed clays of this grade.

Figs. 3 and 4 indicate quantitatively the pronounced effect upon production cost of variations in the alumina and silica content of the clays and in the CaO content of the limestone. Fig. 3 indicates the increase in the amount of limestone and fuel required as the Al_2O_3 content

clays. In compiling the curves (Figs. 3 and 4), composite analyses of a number of actual clays were used for each point on the curves to obtain a normal relationship between Al_2O_3 and SiO_2 , and to give a smooth curve, which at the same time would not be a purely hypothetical one.

The dollar costs (Fig. 4) are relative only, and for any specific case the curves would be raised or lowered on the scale, depending upon whether costs for mining and quarrying, freight and handling, crushing, grinding, furnacing, leaching, reagents, power, fuel, taxes, and other costs determined by local conditions were higher or lower than the costs assumed in preparing the curves.

The limestone curves (broken lines) in Fig. 4 clearly indicate the desirability of high-calcium limestone for use in the process. Some impurities have a very

and toughness of the rock and the character of the overburden, and the amount of water to be handled, are all factors that affect the quarrying or mining cost.

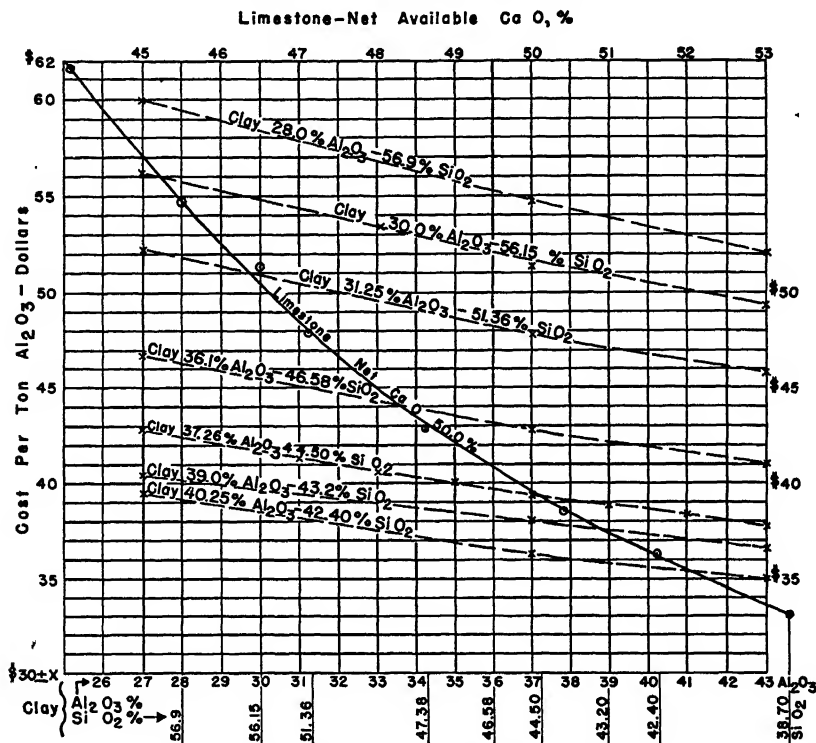


FIG. 4.—RELATIVE COST PER TON Al_2O_3 FROM RAW MATERIALS OF VARYING COMPOSITION.

Limestone curve solid: net CaO constant, clays variable.

Clay curves broken: clays constant, net CaO variable.

Note: Base price (ordinate Fig. 4), is hypothetical and subject to a variable addition ($\pm x$) related to operating costs in a specific case.

adverse effect on recovery of Al_2O_3 , whereas each mol of SiO_2 in the limestone requires 2 mols of CaO, thus reducing the amount of available CaO in the limestone.

Mining or Quarrying Costs

The cost f.o.b. plant of raw materials (ore and limestone) is an important item in production cost. This cost comprises cost of materials in the ground, mining haulage and freight. The depth below the surface, thickness and horizontal extent of the deposits, their shape, regularity in form and in analysis, hardness

Where opencut quarrying is applicable, the cost generally is much lower than underground mining, and the actual cost is determined to a considerable extent by the thickness and character of the overburden and the ratio of ore thickness to that of the overburden. The actual operating cost at the opencut clay pits some years ago averaged \$0.175 per ton including stripping, whereas the cost of underground mining at four underground clay mines was \$0.965 per ton. At eight limestone quarries, operating costs ranged between \$0.115 and \$0.336 per ton. These figures

are cited to illustrate the extent to which local natural conditions may affect the cost of raw materials.

If selective mining must be employed because of the irregularities of the deposits, costs may be two or three times as high as where the deposits are uniform in grade and regular in shape.

Geography

The Ancor process requires only three raw materials in large quantities—ore, limestone and coal (or other fuel). An ideal situation for a plant would be one where all three occur in a restricted area in sufficient quantities and of desirable quality.

Since for high-alumina clay, for example, more than two tons of limestone is required for the process to one ton of clay, the obvious location for the plant from the standpoint of freight costs is at the limestone quarry. In some localities considered for a plant site, the railroad freight on the ore would be considerably more than the cost of the clay in the ground plus the mining cost.

If coal is the fuel to be used for furnacing, the freight will vary between wide limits, dependent upon the length of haul from the coal mine to the plant; often the freight will be more than the cost of the coal at pit mouth. Since the fuel cost is one of the major items in the cost of making alumina by the Ancor process, the geographical location of the plant with respect to the source of fuel is an important consideration.

Of less importance but still a factor in production cost is the freight on supplies; soda ash, grinding media and refractories.

Geographical location would affect the value of by-products, especially those having a low value per ton that would not permit their shipment beyond a limited radius from the plant. Availability of labor, low-cost power, and housing facilities for employees are also geo-

graphical factors that may affect manufacturing costs and the capital outlay required.

Fuel

Most of the cost computations we have made to date have been based on the use of low-ash, high-volatile coal for furnacing. In the cases figured, the fuel cost was usually 20 to 25 per cent of the total production cost although the range was considerably greater. In some localities natural gas or fuel oil may be available at prices that would reduce costs below those possible with coal.

Value of By-products

It is generally believed that alumina cannot be produced from clay or other materials than bauxite at a cost that will be competitive with its manufacture from bauxite unless substantial income can be derived from by-products. The writers do not subscribe to this opinion without reservations. Based upon careful estimates, there are believed to be localities where reserves of raw materials have been proved to occur in large quantities and of high purity within economic radius for bringing them together, and where other economic conditions are such that, in the absence of proof to the contrary, production of alumina from materials other than bauxite would be profitable. This can be proved in one way only—in a plant with equipment of optimum size.

The competitive position of such a plant should be very favorable in comparison with one utilizing high-silica bauxite.

The residue from an Ancor plant is composed mainly of dicalcium silicate with a small admixture of calcium carbonate. It is no secret that this is a desirable raw material for the manufacture of Portland cement. In the pilot-plant work a very good Portland cement was made using this residue for 85 per cent or more of the raw

cement-kiln feed. It is indeed possible that cement manufactured from this residue may produce a cement of superior quality.

There are other possible commercial uses for the residue, and it is believed that research will develop more such uses.

Some raw materials with which Ancor has worked for the production of alumina contain substantial amounts of recoverable by-products. Thus, in making alumina from high-purity nepheline syenite, more than 60 tons of soda ash and 30 tons of potash are recovered per 100 tons of alumina extracted. Other aluminous raw materials with which Ancor has worked from which valuable by-products might be derived are leucite and spodumene.

Without further elaboration, it is apparent that many factors affect the cost of producing alumina by the Ancor process, and that this cost would vary between wide limits in different localities and with the nature of the raw materials. It is evident also that alumina cannot be produced economically from the raw materials considered, except under a combination of favorable factors. Although Ancor has not fully explored all the possibilities, it is believed that such favorable situations have been found in at least two regions where the company has made extensive and careful investigations.

One of these is in South Carolina, where there is an abundance of limestone of high purity containing about 52 per cent net available CaO (after taking care of the contained SiO₂), and considerably less than 1 per cent MgO. Within economical shipping distance, more than 9,000,000 tons of clay containing an average of 35 per cent + alumina was developed by 154 drill holes, and further exploration would certainly develop much more.

On Aug. 1, 1943, Ancor began construction of a plant in South Carolina as agents for and on behalf of Defense Plant Corporation, under a directive of the War production Board. This plant, though designed to

produce only 100,000 lb. of alumina per day, will have equipment of optimum size.

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DISCUSSION

J. E. CONLEY.*—I should like to ask about the relative merits of the concurrent and countercurrent methods of firing the rotary kiln for producing the lime-sinter product. It is my understanding that these two different procedures are being sponsored by Ancor and by T.V.A., respectively. The latter are in connection with the modified Pedersen leaching of lime sinters.

May I inquire as to the size of tests that have been made to date on the sintering and leaching steps of the Ancor process?

Fig. 3 indicates that the consumption of coal per ton of alumina varies directly as the silica content and inversely as the alumina. However, the ordinates are based upon the dry process whereas the flowsheet illustrated in Fig. 1 indicates the use of a wet-slurry feed. What is the type of feed to be used in the semicommercial, pilot-plant tests?

F. R. ARCHIBALD (author's reply).—Adequate consideration of the subject of concurrent vs. countercurrent firing of rotary kilns for producing lime-sinter would require a more lengthy reply than discussion of the present

* Chief, Chemical Engineering Unit, Eastern Experiment Station, U. S. Bureau of Mines College Park, Maryland.

paper warrants. The chief advantages gained by the former procedure are believed to be:

1. Elimination of the sharp peak in material temperature curves characteristic of counter-current cement kilns. This peak occurs in the area of silicate reaction and, in addition to making temperature control difficult, limits the important reactions to a very short kiln length. The practical advantage of lowering and extending the peak through concurrent firing is in aiding temperature control and increasing capacity per unit kiln volume.

2. Minimum formation of undesirable compounds in temperature ranges below 2350°F.

3. Longer period of treatment at and following maximum material temperature, permitting more complete formation and stabilization of desired compounds.

Continuous sintering tests employing the Ancor process have been conducted at a dry kiln-feed rate of one ton per 24 hr. Leaching has been carried out on accumulated sinter at twice the rate of kiln production.

The Harleyville plant, South Carolina, will employ a filtered, wet slurry feed to the preheat kiln as shown on the flowsheet (Fig. 1). Representation of fuel requirements on a dry feed basis as in Fig. 3 was considered more logical for illustrative comparison of fundamental variables concerned. Since apparently it has escaped notice, readers are asked to note that coal requirements shown in Fig. 3 are for dry treatment.

R. MILLER.*—The authors have laid considerable stress upon the geographical location of the raw materials that are required to produce alumina by the lime-sinter, soda-leach process. This is very commendable in view of the large ratio of raw materials to product in this process. Approximately 12 tons of raw material, clay, limestone and coal, is required per ton of alumina.

The authors have defined an ideal situation for a plant as one where all three raw materials occur in a restricted area in sufficient quantities and of desirable quality. I should like to point out that the ideal location would also include close proximity to the metal-production plant. The advantage of producing a product close to the place where it is consumed is well

illustrated by the Basic Magnesium enterprise. The production of chlorine at the Basic Magnesium plant results in the concomitant production of caustic soda. Originally, it was planned to concentrate the caustic soda liquor and sell it. However, it was found that no market was available for it within economic shipping distance and so the caustic solution is just dumped on the desert.

F. R. ARCHIBALD.—Without going into detailed consideration of heat requirements in sintering dry limestone-clay mixtures of the composition and at the temperatures described, it can be generally stated that theoretical calculations show a heat requirement from 10 to 25 per cent less than for equivalent tonnages of portland cement raw materials.

The variations in reduced heat requirement are occasioned by variable components of portland cement and some disagreement in published heat data for silicate reactions. It is obvious that for high-grade materials there is a lower proportion of calcium carbonate, a lower firing temperature and a greater proportion of exothermic reaction in furnacing for alumina recovery than for manufacture of portland cement.

In the particular case selected by Mr. Miller, the requirement of 1.25 tons coal per ton of alumina is equivalent to 230 lb. per ton of raw material. This is about 15 per cent less than would be expected in an efficient dry-process cement plant, and in keeping with the statement of general comparison.

As a general note on the coal requirement for the process as a whole, attention is called to the fact that Fig. 3 represents coal for sintering of dry raw materials only. Additional coal is required for making steam, heating wash water, maintaining solution temperatures, and general heating.

A. M. SHORT.*—Four general clay areas of the United States have been mentioned, where resources are available in sufficient quantities to warrant the establishment of alumina plants of pilot or commercial size. In general, where are these areas?

C. F. JACKSON (author's reply).—We would not limit the number to four areas where ade-

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*Mineral Technologist, Missouri Pacific Lines, St. Louis, Missouri.

quate reserves of high-purity raw materials exist, since exploration by private concerns and exploration at Government expense, the results of which have not been published, may have revealed others.

Of the four areas we selected, the one in South Carolina and Georgia appears, on the basis of available data, to be the most promising. Others are, respectively, in East Central United States, Central United States, and in the Northwest. Other areas would require extensive exploration to determine their potentialities.

D. R. WILLIAMS.*—The Monolith Portland Midwest Co. is constructing, for the Defense Plant Corporation, at Laramie, Wyo., a large semicommercial plant for the production of alumina from anorthosite, using the soda-lime-

sinter process perfected by the company. This plant is designed after a small test plant, large enough to process several tons of raw material, that was operated for over a year. Construction is well under way and we expect to be operating before the first of next year.

The Monolith Portland Midwest Co. manufactures portland cement and the soda-lime-sinter process to be used is patterned after standard cement-plant practice. The flowsheet includes the quarrying of limestone and anorthosite, wet grinding, slurry blending, drying, sintering, leaching, countercurrent decantation, filtering (solid residue returned to cement plant for use as cement raw material), purification of liquor, precipitation of crystalline aluminum hydrate and calcining to alumina.

Unlimited quantities of anorthosite have been found in the Laramie Mountains. This rock of pre-Cambrian age is exposed over an area of nearly 400 square miles.

* Chief Chemist, Monolith Portland Midwest Company, Laramie, Wyoming.

Extraction of Alumina from Clays by the Lime-sinter Modification of the Pedersen Process

BY RAYMOND L. COPSON,* JOHN H. WALTHALL,* AND TRAVIS P. HIGNETT*

(New York Meeting, February 1944)

IN October 1942, the War Production Board requested the Tennessee Valley Authority to undertake investigations to determine the feasibility of producing alumina suitable for reduction in aluminum cells, from clays and other domestic materials, by a lime-sintering, soda-ash leaching process. The work was undertaken by the chemical engineering staff of the Authority under the general direction of the War Metallurgy Committee of the National Academy of Sciences.

The investigation included small-scale tests to determine the most suitable conditions for the process, and construction and operation of a pilot plant to obtain data for evaluation of the process and for design of a plant. The results of this investigation are described in the present paper.

SOURCES OF ALUMINA

Alumina for the commercial production of aluminum is obtained from bauxite by the Bayer process. The tremendous demand for aluminum for wartime uses is causing rapid exhaustion of the high-grade bauxite deposits in the United States. On the other hand, there is an abundance of aluminous materials such as clay and lower grades of bauxite, which are not suitable for treatment by the Bayer process because of their high silica content.

The Tennessee Valley Authority has

conducted research and pilot-plant work for more than 5 years on methods for the production of alumina from clay and low-grade bauxite. Particular attention has been given to the high-grade white kaolin found in Carroll County, Tennessee. Exploratory drilling has demonstrated that at least $4\frac{1}{2}$ million tons of kaolin containing in excess of 34 per cent Al_2O_3 is available in this area by strip-mining methods. It has been estimated that hundreds of millions of tons of clay of similar quality occur in the Tennessee Valley region.

THE PROCESS

The process is illustrated in the flow-sheet (Fig. 1), and consists essentially of the following steps:

1. Heating a mixture of clay and limestone to form a sinter containing calcium aluminate and dicalcium silicate.
2. Leaching this sinter with a dilute sodium carbonate solution, to form a sodium aluminate solution and a calcium carbonate, calcium silicate residue, which is discarded.
3. Treating the sodium aluminate solution with carbon dioxide to precipitate aluminum trihydrate and regenerate the sodium carbonate solution, which is recycled.
4. Heating the aluminum trihydrate to produce alumina.

The process was considered promising because of the abundance and cheapness of the two raw materials, clay and limestone; and because, as compared with an acid process, smaller amounts of critical

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* Tennessee Valley Authority, Wilson Dam, Alabama.

materials would be required in plant construction.

The heating of an aluminous material with lime, as in step 1, to yield a product containing calcium aluminate and calcium

ore, and coke to produce calcium aluminate slag and iron. The slag was low in silica, and the CaO and Al_2O_3 were present in proportions that made the predominating aluminate $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

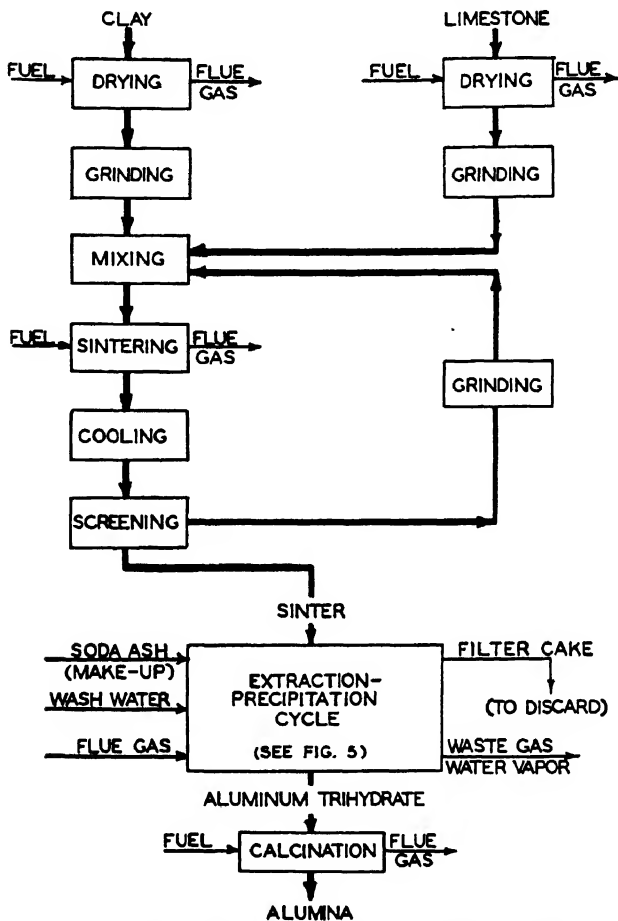


FIG. 1.—FLOW SHEET OF MODIFIED PEDERSEN PROCESS.

silicate is a well-known operation; and many investigations have been made of the extraction of alumina from a sinter or slag containing calcium aluminate, as in step 2. Of these previous investigations, only the following need be mentioned:

Pedersen¹ smelted together bauxite or other aluminous material, limestone, iron

Pedersen² leached the calcium aluminate slag with a 3 to 8 per cent sodium carbonate solution containing about 10 per cent of the total soda as sodium hydroxide, and stated that sodium aluminate solutions were obtained containing SiO_2 to the extent of less than 0.1 per cent by weight of the Al_2O_3 content. He precipitated aluminum tri-

¹ H. Pedersen: British Patent 232930 (April 23, 1924).

² H. Pedersen: U. S. Patent 1618105 (Feb. 15, 1927).

hydrate from this solution by autoprecipitation, and then carbonated the solution to leave about 10 per cent of the total soda as sodium hydroxide, thus regenerating a solution of the composition desired for the extraction step. By his technique, about two thirds of the dissolved alumina was said to be precipitated per cycle, and the ratio of SiO_2 to Al_2O_3 was found to be lower in the precipitate than in the solution.

Seailles and Dyckerhoff³ mixed aluminous material containing silica with limestone in the proportions to provide 2 mols of CaO per mol of SiO_2 , 1.3 to 2.0 mols of CaO per mol of Al_2O_3 , 1 to 2 mols of CaO per mol of TiO_2 , and 2 mols of CaO per mol of Fe_2O_3 . The mixture was calcined, and the calcium aluminate was extracted with water.

Since it was proposed to sinter the aluminous material (clay) with lime (limestone), and to recover alumina from the sinter essentially by the method used by Pedersen,² the process was called the lime-sinter modification of the Pedersen process.

Through the War Metallurgy Committee, unpublished material describing research on related processes was made available to the T.V.A. staff.

In the investigation of step 1, it was necessary to determine the optimum proportions of raw materials, and conditions of sintering, to produce sinter containing the maximum proportion of alumina soluble in dilute sodium carbonate solution. It also was necessary to determine the type and capacity of equipment suited for the production of sinter.

In the investigation of steps 2 and 3, it was essential to determine whether the Pedersen procedure, which was developed for recovery of alumina from a slag made from bauxite low in silica, could be applied to a sinter made from clay with resultant production of aluminum trihydrate of high purity and desirable physical properties.

³ J. C. Seailles and W. R. G. Dyckerhoff: U. S. Patent 2248826 (July 8, 1941).

It also was necessary to establish the design and capacity of equipment for conducting the process on a large scale.

Study of the final step of the process was omitted, since the heating of aluminum trihydrate is a part of the Bayer process for the production of alumina.

PRELIMINARY SINTERING TESTS

A typical analysis of the clay from Carroll County, Tennessee, which was used in most of the small-scale experiments and in all of the pilot-plant work, is given in Table 1. An Arkansas clay also was used in small-scale sintering tests, and was found to be similar to the Tennessee clay.

The limestone used in the pilot-plant work was selected on the basis of tests described in the following paragraphs. It was obtained from a quarry near Sheffield, Alabama, and its purity is shown by the typical analysis in Table 1.

TABLE 1.—*Analyses of Clay and Limestone*
PER CENT BY WEIGHT

Material	Al_2O_3	CaO	SiO_2	TiO_2	Fe_2O_3	MgO	Ignition loss	Total
Dry clay.....	38.4	0.5	44.0	2.4	0.7	0.3	14.4	100.7
Calcined clay	44.5	0.6	51.0	2.8	0.8	0.3	0.0	100.0
Limestone...	0.1	55.2	0.6	0.0	0.1	0.8	43.5	100.3

The fineness of both the clay and the limestone was varied to some extent during the experimental work. Early experiments indicated that both materials should be ground to pass a 100-mesh screen. During the later part of the pilot-plant operation, the clay was ground until 65 per cent passed through a 200-mesh screen, and the limestone until 90 per cent passed through a 325-mesh screen.

Preliminary small-scale sintering tests were made either (1) by heating dry mixtures of clay and limestone in a platinum boat in an electric tube furnace; or (2) by preparing briquettes from moist mixtures of clay and limestone, drying the briquettes,

and then sintering them in an electric muffle furnace. The best sinters were hard and dense. They started to "dust" within a few minutes after removal from the fur-

sodium carbonate solution for 30 min. at 50°C., or for 15 min. at 65°C. The quantity of solution was sufficient to provide at least 1.6 mols of Na_2O as sodium carbonate

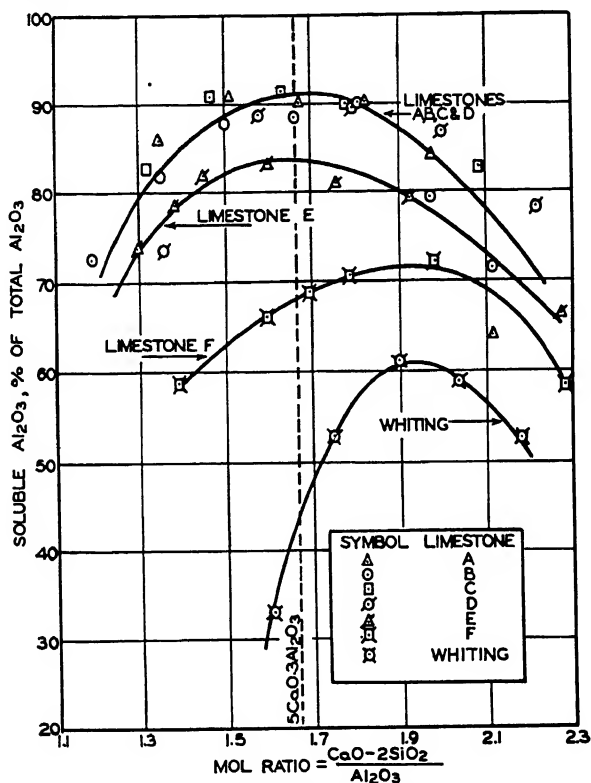


FIG. 2.—EFFECT OF MOL RATIO OF CaO TO Al_2O_3 ON RELATIVE SOLUBILITY OF Al_2O_3 IN LIME-CLAY SINTER.

nace, and in less than an hour had disintegrated to a powder consisting of particles 1 to 25 microns in size. The "dusting" or disintegration of the sinter has been observed by other experimenters, and is characteristic of sinters that contain dicalcium silicate. Apparently the phenomenon is caused by transition of the dicalcium silicate from the beta to the gamma modification, which takes place with an increase in volume.

The sinters were evaluated by determining the content of total and soluble Al_2O_3 . The latter was determined by extracting the disintegrated sinter with a 3 per cent

for each mol of Al_2O_3 in the sinter. The reactions occurring during dissolution of the Al_2O_3 are discussed in the section on leaching and precipitation.

In proportioning clay and limestone, Seailles and Dyckerhoff³ made an allowance for TiO_2 and Fe_2O_3 . The percentages of these constituents in the clay and calcareous materials were low, and they are disregarded in the discussion of the composition of the lime-clay mixtures and sinters prepared therefrom.

In the first series of experiments, clay and reagent-grade calcium carbonate were mixed in proportions to provide 2 mols of

CaO for each mol of SiO_2 , plus $1\frac{3}{8}$ mols of CaO for each mol of Al_2O_3 . The results of these tests showed that sinter in which 85 to 90 per cent of the total Al_2O_3 was soluble

The optimum ratios of limestone to calcined clay varied considerably with the different limestones. However, for the purer materials, limestones A, B, C, and D,

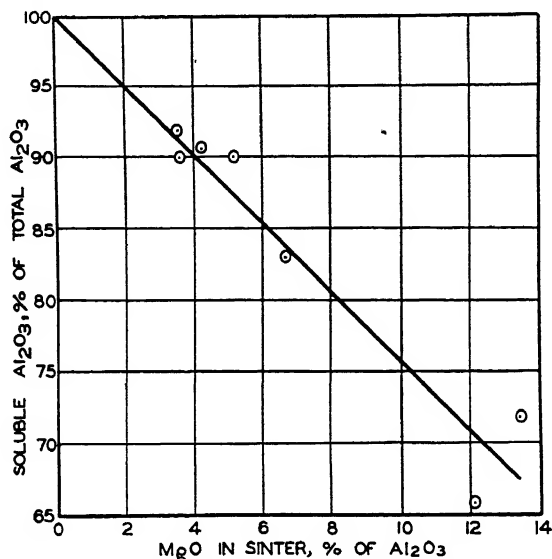


FIG. 3.—EFFECT OF MgO CONTENT ON SOLUBILITY OF Al_2O_3 IN LIME-CLAY SINTER. Line corresponds to 1 mol of insoluble Al_2O_3 per mol of MgO in sinter.

could be prepared both from a dry, intimate mixture of clay and limestone, and from a briquetted mixture. Sinter containing the maximum proportion of soluble Al_2O_3 was obtained when the mixture was heated at 1365° to $1390^\circ\text{C}.$ for at least 30 min. Reasonable variations in the time of heating to the sintering temperature, and in the rapidity of cooling after removal from the furnace, were found to exert no appreciable effect upon the soluble alumina content of the sinter.

The next series of experiments was made with limestones from several different sources. Each limestone was mixed with calcined clay in proportions that were varied through a sufficient range to determine the composition yielding the maximum percentage of soluble alumina. The mixtures were sintered for 90 min. at $1365^\circ\text{C}.$ The results of these tests are shown in Fig. 2.

the optimum weight ratio averaged 2.49 lb. of limestone per pound of calcined clay, and the optimum mol ratio was such as to supply 2 mols of CaO per mol of SiO_2 , and $1\frac{3}{8}$ additional mols of CaO per mol of Al_2O_3 . For the less pure materials, limestones E and F, the optimum weight ratios were 2.67 and 2.83, and the optimum mol ratios were 1.60 and 1.97, respectively. The data show that the proportion of limestone to clay is critical if sinter of nearly the maximum soluble alumina content is to be produced. The calculated composition of sinters corresponding to the optimum proportions of limestone and clay (Fig. 2) are given in Table 2.

Experiments also were made with whitening as a source of lime, and the results are included in Fig. 2 and Table 2. The whitening was of extreme fineness, all of it going through a 300-mesh screen. However, as the data show, the best sinter made with

whiting was relatively low in alumina solubility.

The solubility of the alumina in the best sinters made from the various limestones,

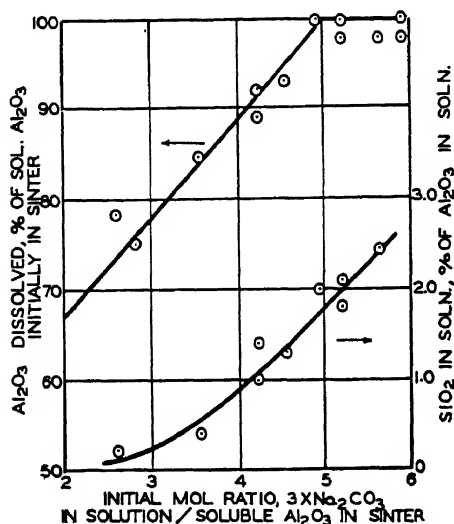


FIG. 4.—EFFECT OF $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ RATIO ON DISSOLUTION OF Al_2O_3 AND SiO_2 .

Upper line is drawn according to the theory outlined in the text; lower curve represents average of observed data.

and from whiting, apparently was related to the MgO content of the raw materials. In Fig. 3, data are plotted for the sinters of optimum composition, the graph indicating that the soluble Al_2O_3 content of the best sinters decreased as the MgO content increased, approximately in the proportion of 1 mol of Al_2O_3 per mol of MgO .

PREPARATION OF SINTER

In the pilot plant, sinter was prepared in a 40-ft. rotary kiln having an inside diameter of 30 in. The kiln was oil-fired, and the burner was adjusted to give a flame 10 to 12 ft. long. The kiln was lined with a high-alumina firebrick.

Two methods were used in preparation of most of the mixture supplied to the kiln. In one method, the raw clay was ground with limestone in an edge runner, water

being added until the mix had a smooth consistency; the mixture then was transferred to an extrusion machine, extruded through a 1-in. round die, and the extruded product was cut in short lengths. In the other method, weighed amounts of the dried and finely ground clay and limestone were mixed in a rotating batch mixer; the mixture was tested and, after its composition had been adjusted, if necessary, was processed in a ball mill for 15 min. The second method was preferred because it was simpler and permitted more accurate control of the composition of the mixture.

The prepared charge was shoveled into the kiln by hand, at an average feed rate of about 350 lb. per hour. The rate at which the material passed through the kiln was varied by changing the speed of rotation. Best results were obtained with a kiln speed of 0.5 r.p.m., and at this speed the average time of passage through the kiln was estimated at 3 hours.

The temperature of the sinter in the hottest part of the kiln was held between 1380° and 1390°C ., as measured by an optical pyrometer. Within this temperature range, there was a tendency for rings to form in the hot zone of the kiln. However, when a small proportion of sinter was recycled in the kiln feed, the rings were soft and either fell or could be rodded from the kiln wall without difficulty. At temperatures above 1390°C ., difficulty with ring formation was accentuated, whereas at temperatures below 1380°C . the sinter was not of the desired quality.

The sintered product was discharged from the kiln in the form of flattened balls or rolls, approximately 2 to 8 in. in diameter. These were placed upon heavy, horizontal screens and allowed to cool for about 3 hr. During this period the sinter disintegrated or "dusted," as described above. It then was screened on a vibrating screen, and the material coarser than 20-mesh, which amounted to less than 2 per cent of the total, was returned to the kiln. The

minus 20-mesh product was ready for extraction.

With good operation the dust loss from the pilot-plant kiln averaged about 12 per cent. By improving the method of charging and by installation of dust-collecting

According to Eq. 2, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is first converted to $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, which is then dissolved according to Eq. 3. Thus, when 2 mols of Na_2CO_3 is provided for each mol of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, two thirds of the Al_2O_3 will be in solution, and the sodium alumi-

TABLE 2.—*Sinters of Optimum Composition*

Limestone	Weight Ratio of Limestone to Calcined Clay	Mol Ratio of CaO to Al_2O_3 in Sinter ^a	Composition ^b of Sinter, Per Cent by Weight						Soluble ^c Al_2O_3 , Per Cent of Total Al_2O_3
			SiO_2	CaO	TiO_2	Fe_2O_3	MgO	Total Al_2O_3	
A, B, C, and D.....	2.49	1.67	21.5	57.3	1.3	0.4	0.8	18.8	91
E.....	2.67	1.60	22.2	57.3	1.4	0.4	1.2	17.5	83
F.....	2.83	1.97	21.1	58.1	1.2	0.5	2.4	17.5	72
Whiting.....	2.76	1.90	20.7	57.1	1.2	0.4	2.1	17.6	66

^a After allowing CaO for $2\text{CaO} \cdot \text{SiO}_2$.

^b Calculated from analyses of limestone and clay.

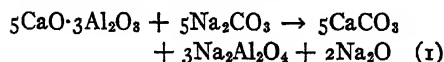
^c By extraction with an excess of 3 per cent sodium carbonate solution for 30 min. at 50°C.

equipment, it is estimated that this loss could be decreased to 5 per cent or less.

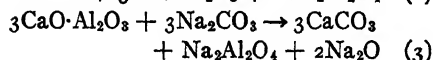
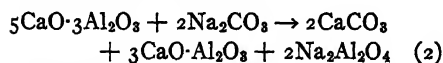
LEACHING AND PRECIPITATION

The action of sodium carbonate solution on the lime-clay sinter was studied in a series of experiments, in which disintegrated sinter was agitated for 15 to 30 min. at 60° to 80°C. with various proportions of a 3 per cent sodium carbonate solution.

For sinter of approximately the optimum composition as described above, it may be assumed that the soluble alumina is in chemical combination principally as $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. The following over-all reaction therefore may be postulated:



Thus when 5 mols of Na_2CO_3 is provided for each mol of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, a solution is produced in which 40 per cent of the total soda is present as free Na_2O (i.e., as sodium hydroxide). Furthermore, it may be postulated that the over-all reaction takes place in two steps, as follows:



nate solution will contain no free Na_2O . Three additional mols of Na_2CO_3 then is required to dissolve the remaining one third of the Al_2O_3 .

The observed experimental data are plotted as points in the upper part of Fig. 4. The line in the upper part of Fig. 4 represents the theoretical relationship between the percentage dissolution of the Al_2O_3 and the mol ratio of Na_2CO_3 to $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, as computed from the foregoing equations. The range covered is from 2 to 5 mols of Na_2CO_3 per mol of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. The points representing the observed data are in excellent agreement with the line derived from theory.

The lower curve in Fig. 4 indicates the silica content of the solutions from the same series of experiments. The data show that, as the extraction of the soluble alumina from the sinter approached 100 per cent, the ratio of SiO_2 to Al_2O_3 in solution increased sharply.

It was apparent that a countercurrent extraction procedure might be effective as a means of dissolving nearly all of the soluble Al_2O_3 , while also producing a sodium aluminate solution of low silica content. In a two-stage, countercurrent extraction, fresh sodium carbonate solution

is agitated with partly extracted sinter, and almost complete dissolution of the alumina should be obtained. The partly saturated solution then is agitated with fresh sinter, and only part of the alumina is dissolved. Because of contact with the excess of sinter, the final solution should be low in silica.

The two-stage, countercurrent procedure was tested in equipment capable of handling about 10 gal. of solution per batch. The equipment consisted of a steel tank provided with an agitator, for the extraction steps; a shallow steel tank with a perforated false bottom covered with cloth, which was used as a suction filter; and a stainless-steel tank provided with a manifold for bubbling a mixture of carbon dioxide and air through the solution, for the precipitation step. Using this equipment, a large number of complete extraction and precipitation cycles were performed.

In the course of this work, it was found advantageous to add a small portion of the sinter toward the end of the "half-saturation" step, thus considerably decreasing the amount of silica in the solution going to the "saturation" step, and in turn making it possible to produce "saturated" solutions of lower silica content.

A detailed flow diagram of the extraction and precipitation cycle is given in Fig. 5, and a typical cycle is described below:

"Half-saturation" Step.—At the start, tank No. 2A (Fig. 5) contained regenerated sodium carbonate solution. Soda ash was added to bring the total Na_2O content of this solution to 3.4 per cent, calculated as Na_2CO_3 . The solution was heated to about 50°C . The partially leached sludge from the previous cycle was transferred to the extraction tank and the slurry was agitated, usually for 40 min. A small, weighed amount of fresh sinter was added to the slurry (tank 2B, Fig. 5), and the extraction was continued, usually for about 40 min. more. The slurry was filtered, the filter

cake was washed, the filtrate and wash water were collected in tank No. 1 (Fig. 5), and the filter cake was discarded.

Saturation Step.—The "half-saturated" solution was heated to about 40°C . and a weighed amount of fresh sinter was added gradually. Agitation was continued, usually for about 30 min., and the slurry then was filtered and washed. The solution was collected in the precipitation tank, and the partially extracted filter cake was used in the next cycle.

Precipitation Step.—Keeping the solution at the desired temperature, usually about 50°C ., a mixture of carbon dioxide and air, containing about 20 per cent CO_2 by volume, was bubbled through the solution. The carbonation was continued until titration of a sample of the solution showed that the desired $\text{CO}_2:\text{Na}_2\text{O}$ mol ratio had been reached. Usually some trihydrate from previous precipitations adhered to the tank; otherwise, a small quantity of crystalline aluminum trihydrate from a previous precipitation was added to the solution as seed charge before carbonation. After carbonation, the precipitated aluminum trihydrate was allowed to settle, and the clear or slightly turbid solution was decanted for use in the next cycle. The precipitate was filtered and washed, and the wash water was added to the regenerated solution.

It is understood that the procedures of double extraction and of the addition of a small portion of the extractable material during the "half-saturation" step were used by Pedersen. However, because of the considerable difference in the composition of the aluminous material, the extraction and precipitation methods developed in the present work differed from Pedersen's technique in several important respects.

In treating slag in which the predominating aluminate was $\text{CaO}\cdot\text{Al}_2\text{O}_3$, Pedersen² found that the silica content of the aluminate solution was at a minimum when the initial sodium carbonate solution con-

tained about 10 per cent of the total soda as sodium hydroxide. However, as shown above, when sufficient sodium carbonate is used to dissolve nearly all of the alumina

aluminate solution containing only a small proportion of free Na_2O .

The difference in the composition of the aluminous materials also led to a variation

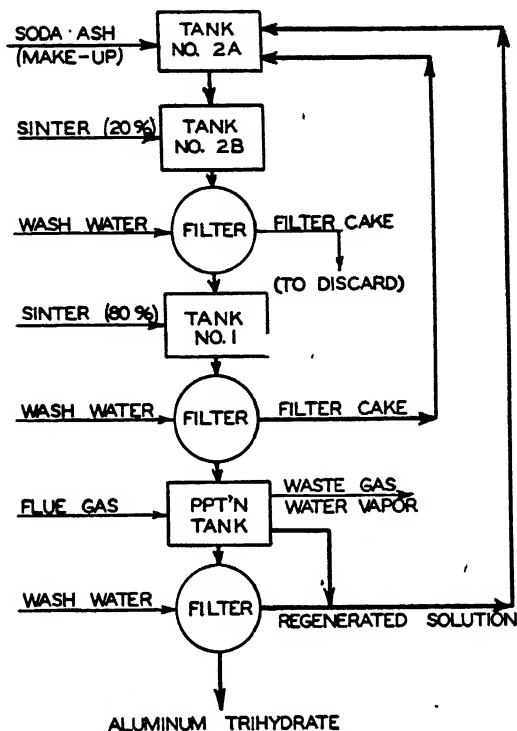


FIG. 5.—FLOWSHEET OF EXTRACTION-PRECIPITATION CYCLE.

from clay-lime sinter in which the predominating aluminate is $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, nearly 40 per cent of the total soda in the resultant solution is present as free Na_2O (sodium hydroxide). Consequently, in this case there appeared to be no advantage in using an original sodium carbonate solution containing sodium hydroxide.

On the contrary, it appeared logical to treat clay-lime sinter with a sodium carbonate solution containing an excess of carbon dioxide; in other words, to use a sodium carbonate-bicarbonate solution. With such a solution, it should be possible to dissolve most of the Al_2O_3 from $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and to produce a sodium

aluminate solution containing only a small proportion of free Na_2O . The difference in the composition of the aluminous materials also led to a variation

from the precipitation technique used by Pedersen. To produce a regenerated sodium carbonate-bicarbonate solution, an excess of carbon dioxide was used in the precipitation step, and almost all of the alumina in the solution was precipitated during each cycle. The results of the intermediate-scale experiments need not be described in detail, since approximately the same results were obtained later in the pilot-plant work described in the following pages. In general, the experiments showed that, under suitable conditions, it was possible to extract about 95 per cent of the soluble alumina content of the sinter, and to produce

sodium aluminate solutions containing SiO_2 to the extent of not more than 0.05 per cent of the Al_2O_3 content. In a number of experiments the amounts of Al_2O_3 and

PILOT-PLANT RESULTS

Data from the intermediate-scale experiments were utilized in designing the pilot plant. The extraction-precipitation cycle of

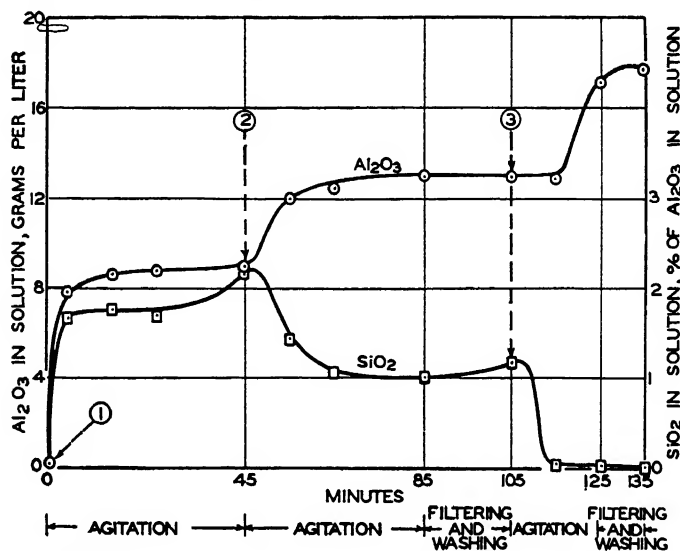


FIG. 6.— Al_2O_3 AND SiO_2 CONTENT OF SOLUTION DURING TYPICAL EXTRACTION.

1. Filter cake from previous cycle added to solution.
2. Sinter added (one fourth).
3. Sinter added (three fourths).

SiO_2 in solution were determined at intervals during the extraction steps. The data of Fig. 6 are typical of the results obtained. Analyses of samples of solution taken at intervals during precipitation showed that the first portion of the alumina precipitate was lower in silica content than that precipitated later; however, the difference was not considered sufficiently great to be of practical importance. Samples of precipitated alumina had the composition shown in Table 3.

TABLE 3.—*Analyses of Alumina*
PER CENT BY WEIGHT, IGNITED BASIS

SiO_2	TiO_2	Fe_2O_3	MgO	CaO	P_2O_5	Na_2O	Al_2O_3^a
0.02	0.00	0.01	0.12	0.09	0.00	0.4	99.4
0.05	0.00	0.01	0.10	0.08	0.00	0.6	99.2
0.08	0.00	0.01	0.12	0.05	0.00	0.4	99.3
0.08	0.00	0.01	0.11	0.07	0.00	0.6	99.1

^a By difference.

the pilot plant was the same as that shown in Fig. 5, but whereas in the intermediate-scale experiments each step was carried out batchwise, in the pilot plant the extraction steps were continuous.

Fig. 7 is a photograph of the pilot plant. The rotary kiln in which sinter was prepared is in the background, the extraction equipment in the center, and the precipitation tanks at the right. Sinter from the kiln was fed continuously to the No. 1 extraction train, which consisted of three tanks arranged for series flow. The slurry overflowing from the tanks passed to the No. 1 rotary filter, which was 3 ft. in diameter and had a 2-ft. wide face. The washed filter cake was discharged to the first of the four tanks of the No. 2 extraction train. A small amount of sinter was fed continuously into the third or fourth tank of this train. The slurry was filtered on the No. 2 rotary

filter, of the same size as the other, and the washed filter cake was discarded. Regenerated sodium carbonate-bicarbonate solution from the storage tanks, in the

drier. The regenerated sodium carbonate solution was returned to the storage tank.

A factor that limited the continuous operation of the extraction unit was the

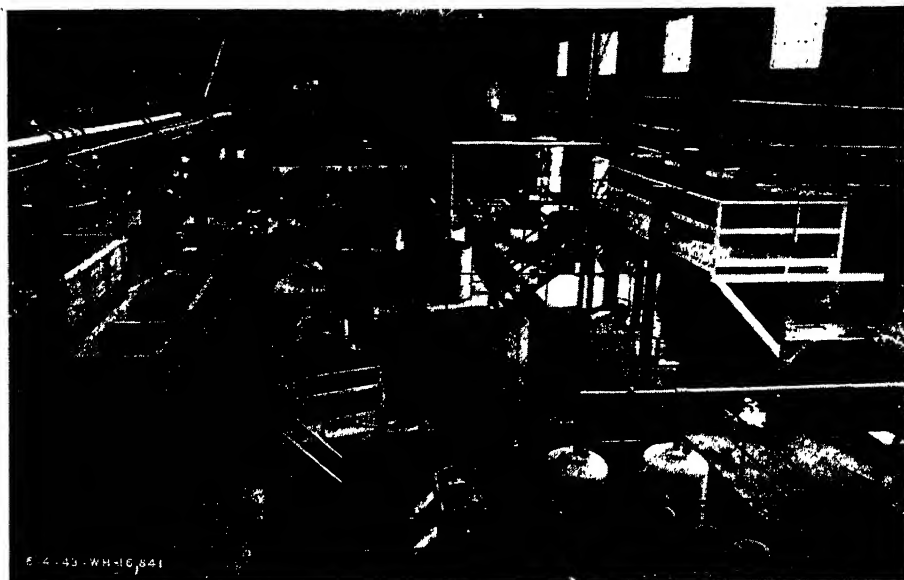


FIG. 7.—PILOT PLANT FOR PRODUCTION OF ALUMINA FROM CLAY BY LIME-SINTER MODIFICATION OF PEDERSEN PROCESS.

center of Fig. 7, passed through the No. 2 extraction train and rotary filter, and then to the No. 1 extraction train and rotary filter. The sodium aluminate solution was stored in a tank, shown in the background in Fig. 7, and was pumped through a plate-and-frame filter to the precipitation tanks, where it was carbonated to precipitate aluminum trihydrate. Each of the three precipitation tanks was steam jacketed and provided with a compressed-air line for agitation. Flue gas was produced by burning oil or carbon monoxide gas in a fire-brick combustion chamber, the gas was cooled by water sprays in two towers, and then was pumped by a Roots blower to manifolds in the precipitation tanks. A wooden tank having a perforated-plate bottom covered with filter cloth was used for dewatering the precipitated aluminum trihydrate, which then was dried in a tray

tendency for a cement to form in the No. 1 filter, necessitating either the cleaning or the replacement of the cloth. The cloth was cleaned by washing with a hot 12 per cent sodium carbonate solution or with a cold 1 per cent hydrochloric acid solution, followed by scrubbing with a wire brush. The life of a cloth on the No. 1 rotary filter did not exceed 40 to 50 hr. No difficulty with formation of cement was experienced in the No. 2 rotary filter.

It was necessary to arrange all piping and troughs used for transporting slurry so that they could be cleaned readily, because gradually they became coated with a layer of solid material.

With the exception of these minor difficulties, the pilot plant was operated satisfactorily. The results may be summarized as follows.

Effect of Ratio of Na_2O and CO_2 to Sinter. When the rates were adjusted so that about 1.4 mols of Na_2O and 1.7 mols of CO_2 was provided in the recycled solution per mol of soluble Al_2O_3 in the sinter, all of the soluble Al_2O_3 was dissolved, and the SiO_2 content of the solution was from 0.1 to 0.3 per cent of the Al_2O_3 content. When the rates were adjusted so that about 1.25 mols of Na_2O and 1.6 mols of CO_2 was provided per mol of soluble Al_2O_3 , about 95 per cent of the soluble Al_2O_3 was dissolved, and the SiO_2 content of the solution ranged from 0.05 to 0.2 per cent of the Al_2O_3 content. During about two weeks of carefully controlled operation, the average SiO_2 content of the solution was approximately 0.05 per cent of the Al_2O_3 content.

Effect of Concentration of Solution.—Within the range from 3.0 to 5.5 per cent, expressed as Na_2CO_3 , variation of the concentration of the solution had no apparent effect on operation of the pilot plant, except that there was less difficulty with cement formation in the No. 1 filter when the more concentrated solution was used.

Effect of Time and Temperature of Extraction.—In the No. 1 extraction train it was found that the silica content of the solution passed through a minimum value, and that close control of both the temperature and the time was necessary to obtain a solution of low silica content. A temperature of about 40°C . and a time of about 30 min. were found satisfactory in pilot-plant operation. In the No. 2 train, the extraction of alumina was greatest at about 50°C ., and little or no increase in the alumina content of the solution occurred when the retention exceeded 20 minutes.

Effect of Amount of Wash Water.—The optimum total amount of wash water was about 12 lb. per pound of Al_2O_3 recovered. Of this amount, about 7 lb. was used at the No. 2 filter, about 3 lb. at the No. 1 filter, and about 2 lb. in washing the precipitated aluminum trihydrate. The loss of soda in the cake discarded from the

No. 2 filter was equivalent to about 0.02 lb. of Na_2CO_3 per pound of Al_2O_3 recovered, a slight additional amount also being contained in the precipitated aluminum trihydrate. About 6 lb. of water was retained in the discarded filter cake, which contained about 50 per cent moisture. The precipitated aluminum trihydrate carried about 2 lb. of water per pound of Al_2O_3 . Consequently, dilution of the solution was equivalent to about 4 lb. of water per pound of Al_2O_3 recovered. This dilution was compensated by evaporation during carbonation and at other points in the cycle.

Carbon Dioxide Requirement and Efficiency of Utilization.—In the carbonation step the percentage of the carbon dioxide absorbed increased as the rate of gas flow was decreased and as the depth of solution was increased. It did not change appreciably, however, with variation in the concentration of CO_2 in the gas or with the temperature of the solution. Under optimum conditions the utilization of carbon dioxide averaged about 65 per cent, and the total carbon dioxide requirement averaged about 1.1 lb. per pound of Al_2O_3 recovered. This is a minor fraction of the CO_2 contained in the flue gas from the sintering kiln, so that part of this gas can be used to supply all of the carbon dioxide required for precipitation.

Alumina Recovery.—All of the Al_2O_3 taken into solution was recovered as precipitate, except for losses in the wet cake discarded from the No. 2 filter, and mechanical losses. These totaled less than 1 per cent of the Al_2O_3 recovered.

Particle Size of Precipitated Aluminum Trihydrate.—The particle size of the precipitated aluminum trihydrate increased as the rate of carbonation was decreased, as the temperature was increased, and as the concentration of the solution was increased. The particle size of the precipitate decreased during the latter part of the carbonation, and in a few instances the fine portion of the precipitate was resus-

pended in the solution of the next carbonation, thus increasing the average particle size. Under representative conditions, when the temperature of the solution was about 65°C. and the time for carbonation was about 20 hr., practically all of the precipitate passed through a 20-mesh screen, and from 10 to 40 per cent passed through a 325-mesh screen.

Composition of Precipitated Aluminum Trihydrate.—When the solution was carbonated until 1.2 to 1.4 mols of CO_2 was in solution for each mol of Na_2O , virtually all of the Al_2O_3 and 80 to 90 per cent of the SiO_2 in solution were precipitated. However, the SiO_2 content of the precipitated aluminum trihydrate averaged higher than that calculated from analyses of the solutions, because of inadvertent contamination.

Desilication of Solutions by Treatment with Lime.—Although a desilication step was not included in the process as originally proposed, some work was done on desilication of the sodium aluminate solution by treatment with lime. The results, although tentative, indicated that by agitating the sodium aluminate solution with about 1 lb. of lime for each 10 lb. of Al_2O_3 in solution, for 30 min. at 70°C., the SiO_2 content of the solution was reduced to less than 0.02 per cent of the Al_2O_3 content. About 10 per cent of the Al_2O_3 was precipitated from solution by such treatment, but this need not represent a loss, since the solid material, containing CaO , Al_2O_3 , and some SiO_2 , could be returned to the process.

SUMMARY AND CONCLUSIONS

The investigation showed that it is feasible, by a method for processing clay characterized by sintering with limestone and leaching with a dilute soda-ash solution, to produce alumina suitable for reduction in aluminum cells. While the process in many respects is similar to methods previously studied by others, it was necessary to develop modifications of the extrac-

tion and precipitation procedures adaptable to the treatment of a clay-lime sinter.

For the process as developed and tested in the pilot plant, the materials requirements are estimated as follows, per ton of Al_2O_3 :

Clay (38 per cent Al_2O_3 , dry basis).....	3.3 tons
Limestone (55 per cent CaO , dry basis).....	7.0 tons
Soda ash (make-up).....	85 lb.
Water.....	3,000 gal.

The rotary kiln used in the pilot plant was too small to permit estimation of the fuel requirements from pilot-plant data. However, by analogy with cement manufacture the fuel requirement for the sintering kiln is estimated at 39,000,000 B.t.u. per ton of alumina. For calcination of the aluminum trihydrate, it is estimated that an additional 8,000,000 B.t.u. will be required per ton of alumina. It is expected that other processing heat requirements can be met by recovery of waste heat from the sintering kiln.

About 12 tons of wet filter cake containing about 50 per cent moisture is discarded for each ton of alumina produced. The dried material, which consists chiefly of dicalcium silicate and calcium carbonate, may be useful in the manufacture of portland cement.

Operation of the pilot plant showed that all steps of the process can be carried out in relatively simple equipment of conventional design. The over-all recovery of alumina is estimated as 80 per cent, the losses being approximately as follows:

	PER CENT
In dust from rotary kiln.....	5
Insoluble Al_2O_3 in sinter.....	9
Soluble Al_2O_3 in filter cake....	5
Other.....	1

Aluminum trihydrate can be precipitated so that all of it passes a 20-mesh screen and about 10 per cent passes a 325-mesh screen. Indications are that alumina con-

taining 99.3 per cent Al_2O_3 , 0.5 per cent Na_2O , 0.05 per cent SiO_2 , and very small percentages of CaO , MgO , and Fe_2O_3 can be produced in a large plant. Preliminary experiments indicate that by agitation of the sodium aluminate solution with lime, the SiO_2 content of the alumina can be lowered to 0.02 per cent if desired—about 200 lb. of lime per ton of alumina would be required for this step.

It was concluded that the process is promising and deserves consideration for further development on a larger scale.

ACKNOWLEDGMENT

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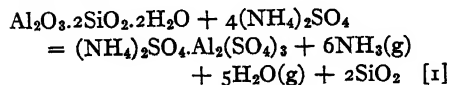
The Ammonium Sulphate Process for Production of Alumina from Western Clays

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(New York Meeting, February 1944)

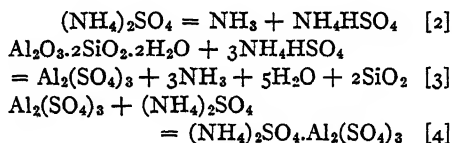
THE ammonium sulphate process for recovering alumina from clays was proposed by Rinman, Buchner, and others many years ago, and more recently various modifications have been investigated both here and abroad.¹⁻¹⁹ The process, as it is being investigated by the Bureau of Mines, involves the following essential steps: (1) sulphating the alumina in the clay by baking with ammonium sulphate at approximately 400°C., (2) leaching with water to extract aluminum sulphate and ammonium sulphate, (3) crystallization of ammonium alum, (4) conversion of the alum to aluminum hydroxide by the ammonia gases given off during the baking, and (5) calcining the aluminum hydroxide to alumina.

The over-all reaction between kaolinite (the most important alumina mineral in most clays) and ammonium sulphate during the baking step may be expressed as follows:



There is definite evidence, as is shown later, that the aluminum occurs in the baked

product as anhydrous ammonium alum rather than as aluminum sulphate, provided the baking temperature is not much above 400°C. It is probable that the reaction takes place in the following steps:



In one modification of the process, the ammonium sulphate is first decomposed according to Eq. 2, and the clay is treated with the resultant ammonium acid sulphate.

Reaction 1 is highly endothermic. On the basis of the best available data, the following values have been estimated for the changes in heat content and free energy in calories per mol:

$$\begin{aligned} -\Delta H &= 331,040 - 34T \\ -\Delta F &= 331,040 - 78.3T \log T - 671.8T \end{aligned}$$

The heat required at 25°C. is 320,900 cal. per mol, or 5650 B.t.u. per pound of alumina. The theoretical equilibrium pressure of NH_3 , based on the free-energy equation given above, increases very rapidly as the temperature rises above 300°C., and reaches one atmosphere at 435°C.

Ammonium alum solutions are almost ideal for crystallization. A saturated solution of ammonium alum contains 126 grams of Al_2O_3 per 1000 grams of water at 90°C. and only 16.5 at 20°C.²⁰ Hence most of the alum crystallizes out when the

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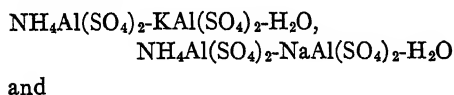
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¹ References are at the end of the paper.

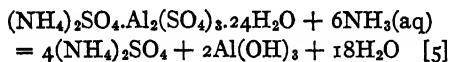
solution obtained by leaching the baked product with hot water is cooled to room temperature. The solubility of ammonium alum is decreased by an excess of either ammonium sulphate or aluminum sulphate, the effect being greater for ammonium sulphate.²¹

Potash, soda, and ferric iron are the only impurities dissolved in leaching that crystallize with the alum to any appreciable extent. The distribution between the solid and liquid phases at 25°C. for the systems



has been studied by Hill and Kaplan.²¹ They found the ratio of potassium alum to ammonium alum in the liquid and solid phases to be almost identical, but they report that sodium alum and ammonium alum do not form solid solutions at 25°C. It was found in this investigation, however, that appreciable amounts of both potash and soda are present in the ammonium alum crystals, but they are eliminated from the alumina in the precipitation of aluminum hydroxide. Hill and Kaplan also found that ammonium alum and ferric ammonium alum form a continuous series of solid solutions. It is difficult, therefore, to keep iron out of the ammonium alum crystals unless the iron is first reduced.

Most sulphate processes for treating clays involve thermal decomposition of aluminum sulphate. In the ammonium sulphate process, however, the ammonia gases evolved during baking are used to convert the alum to aluminum hydroxide, according to the following reaction:



The problem is to produce a precipitate

that can be settled and filtered readily, for unless the proper conditions are maintained the precipitate is gelatinous. If the alum is added to an ammoniacal solution as solid crystals and the pH is maintained sufficiently high during precipitation, the aluminum hydroxide settles and filters readily. The filter cake usually contains only about 25 per cent of solids, which is roughly equivalent to the weight ratio corresponding to replacement of ammonium alum by aluminum hydroxide in the original alum crystals. Some improvement in filtering technique may be possible, but a large proportion of free water seems to be an inherent characteristic of the precipitate.

The filtrate from the precipitation of aluminum hydroxide is evaporated to recover the ammonium sulphate; reaction 5 shows that the amount of ammonium sulphate formed during the precipitation is equal to that theoretically required in the baking step.

WESTERN CLAYS

The more important alumina clay deposits of the West are found in Washington, Oregon, Idaho, and California. Recent exploration by the Bureau of Mines²² has shown that the total amount of clay in five of these deposits exceeds 200,000,000 tons. In general, the western clays contain 25 to 35 per cent Al_2O_3 , 3 to 6 per cent Fe_2O_3 , 1 to 2 per cent TiO_2 , and less than 0.5 per cent CaO , MgO , K_2O , or Na_2O .¹ Most clays contain small amounts of undecomposed feldspars and other aluminum minerals from which the aluminum is not extracted by acid processes. The "available alumina" (that is, the alumina soluble in hot 20 per cent sulphuric acid solution after the clay is dehydrated by calcining at 700°C.) usually constitutes 90 to 98 per cent of the total alumina, and is a useful guide as to the maximum amount of alumina that may be extracted by the ammonium sulphate process.

EXPERIMENTAL RESULTS

Ammonium Sulphate Bake

To determine the more important factors affecting the ammonium sulphate bake, a number of small-scale tests were made on a sample of Utah County clay containing 32.3 per cent total Al_2O_3 and 24.8 per cent available Al_2O_3 . Ten grams of 65-mesh clay was mixed with dry ammonium sulphate and the minimum amount of water required to give a uniform paste; the mixture was dried in a drying oven and baked in an electric muffle furnace, and the baked product was leached at 80°C . with 200 ml. of 1 per cent sulphuric acid solution and washed at 80°C . with 200 ml. of water. The results are summarized in Table 1.

TABLE 1.—*Effect of Temperature and Duration of Bake on Extractable Alumina*

Mols (NH_4) $_2$ SO_4 per Mol of Available Al_2O_3	Temper- ature, Deg. C.	Time, Hr.	Extraction, Per Cent of Available Al_2O_3	Mols (NH_4) $_2$ SO_4 per Mol Al_2O_3 in Extract
3.0	400	2.0	69.1	0.95
		4.0	67.9	1.00
4.0	350	1.0	62.3	1.82
		2.0	70.5	1.52
		3.0	79.3	1.22
3.0	400	2.0	69.1	0.95
3.9	400	2.0	83.1	
4.8	400	2.0	94.4	1.06
4.0	450	1.0	79.2	1.01
		2.0	82.0	0.90
		3.0	86.0	0.81
4.0	550	2.0	86.4	0.0
		2.0	98.6	1.11
5.0	385	2.0	101.0	1.05
	400	2.0	100.0	1.03
	415	2.0	102.0	1.01
	430	2.0	99.5	0.88
	445	2.0	101.2	0.48

The data in Table 1 show that all the available alumina can be extracted in 2 hr. at temperatures above 360°C . provided an adequate excess of ammonium sulphate is used. The excess is required because other constituents of the clay besides alumina are also sulphated and because a certain amount of ammonium sulphate is volatilized before it can react. The mol ratios in the last column of Table 1 show rather

clearly that the soluble alumina in the baked product occurs as anhydrous ammonium alum rather than as aluminum sulphate when the baking temperature is in the neighborhood of 400°C . For example, when the charge contains more than 4 mols of ammonium sulphate per mol of available alumina, the excess slowly sublimes off and the baked product contains one mol of ammonium sulphate per mol of aluminum sulphate even after prolonged baking. Similarly, with a deficiency of ammonium sulphate in the charge, only about three fourths of the ammonia present is evolved, and approximately equimolecular proportions of ammonium sulphate and aluminum sulphate remain in the baked product.

Tests covering a wider temperature range have shown that the extraction of alumina is virtually constant for baking temperatures between 400° to 650°C .; above 650°C ., the extraction decreases, owing to decomposition of the aluminum sulphate.

Particle Size

The effect of size of grind varies considerably with different clays. Those with a soft, clayey texture usually give almost as good extraction at minus 20-mesh as at minus 65-mesh, while hard, shaly clays must be ground through 65-mesh, or even 100-mesh, to give satisfactory extraction. This is shown by the data in Table 2; the Hobart Butte and Lewiston clays are

TABLE 2.—*Effect of Particle Size on Extraction of Alumina from Several Clays*

Size, Mesh	Extraction of Available Al_2O_3 , Per Cent		
	Hobart Butte	Lewiston	Molalla
— 20	43.2		
— 28			
— 35			77.7
— 65	68.5	54.3	79.4
— 100	83.1	90.0	81.8

hard, while the Molalla clay is comparatively soft.

Method of Mixing Charge

The intimacy with which the clay and ammonium sulphate are mixed has an appreciable effect upon the results. Mixing the ammonium sulphate and clay with water to form a paste before baking gives better results than a dry-mixed charge; for example, two comparative tests with dry and wet mixing gave extractions of 68.7 and 87.2 per cent, respectively.

Decomposition of Ammonia in Baking

One of the most important questions concerning the ammonium sulphate process is the loss of ammonia by decomposition during baking. To measure the extent of decomposition, mixtures of 5 grams of minus 65-mesh Molalla clay, containing 29.0 per cent total and 28.1 per cent available Al_2O_3 , and 6 grams of minus 65-mesh C.P. ammonium sulphate (3.3 mols $(\text{NH}_4)_2\text{SO}_4$ per mol available Al_2O_3) were heated in an electric tube furnace. The ammonia in the charge, in the effluent gases, and in the residue was carefully determined. The results of the tests are given in Table 3.

TABLE 3.—*Effect of Temperature on Loss of Ammonia*

Temperature, Deg. C.	Distribution of Ammonia, Per Cent			
	In Absorption Bottles	In Residue	Ac- counted For	Unac- counted For
20		100.		
100	0.078	100.16	100.24	
200	1.015	98.84	99.86	
300	51.93	47.62	99.55	0.45
325	58.14	40.39	98.53	1.47
350	72.57	25.85	98.42	1.58
375	73.23	25.11	98.34	1.66
400	76.11	22.41	98.52	1.48
400	76.12	22.41	98.53	1.47
400	76.22	22.21	98.43	1.57
425	76.44	21.73	98.17	1.83
450	76.62	19.48	96.10	3.90

The ammonia unaccounted for, which is presumed to have been lost by dissociation or oxidation, was negligible below 300°C.,

was virtually constant from 325° to 400°C., and increased above 400°C. The 1.5 per cent loss at 400°C. is equivalent to approximately 33 lb. per ton of available alumina.

Some similar tests were made on a somewhat larger scale in an electrically heated rotating iron tube 3 in. in diameter. Mixtures of 100 grams of Utah County clay, containing 29.0 per cent total and 25.8 per cent available alumina, and ammonium sulphate were baked at 380° to 400°C., with the results shown in Table 4.

TABLE 4.—*Effect of Proportion of Ammonium Sulphate in the Charge on Ammonia Recovery and Alumina Extraction*

Time, Min.	Mols $(\text{NH}_4)_2\text{SO}_4$ per Mol of Available R_2O_3	Ammonia Accounted For, Per Cent	Extraction of Available Al_2O_3 , Per Cent
50	3.0	99.6	61.5
50	4.0	99.9	79.4
60	4.33	98.9	89.8
65	4.66	99.2	93.9
95	5.0	98.9	99.0

The data show that only about one per cent or less of the ammonia was lost by oxidation or decomposition and that with a sufficient excess of ammonium sulphate virtually all the available alumina was made extractable. The loss of ammonia in the last test of Table 4 corresponds to 37 lb. per ton of alumina extracted.

Pilot-plant Tests on Ammonium Sulphate Bake

To determine the ammonia losses that might be expected under actual operating conditions, pilot-plant tests on the ammonium sulphate bake were made in an eight-hearth experimental Herreshoff furnace, 36-in. inside diameter and 6½ ft. high. The furnace was direct-fired by means of inspirator-type, natural-gas burners on the six lower hearths. Each burner was placed at the end of a refractory

firing tube 8 in. in diameter and 3 feet long, in order to prevent excessive flame temperatures within the furnace.

The furnace gases passed through a water-sprayed dust chamber and then through three large sewer-tile scrubbing towers packed with 3-in. quartz pebbles, through which dilute sulphuric acid was circulated. Part of the solution was bled continuously to calibrated measuring and sampling tanks. From the scrubbers the

percentage of alumina made soluble is given in Table 5.

The best recovery of ammonia was in test 5, in which the furnace temperatures were lowest; and the poorest was in test 3, in which the furnace temperatures were highest. The 3.8 per cent loss of ammonia in test 5 corresponds to 140 lb. per ton of extractable alumina. The mol ratios of $(\text{NH}_4)_2\text{SO}_4$ to Al_2O_3 in the leach solutions show that the product was overbaked in

TABLE 5.—*Tests in Herreshoff Furnace on Ammonium Sulphate Bake*

Test Number	2	3	4	5	6
Temperature, (deg. C.): hearths 3 to 7, inclusive,					
Hearth: Average.....	370	400	373	363	382
Maximum.....	420	460	412	410	450
Minimum.....	295	340	340	310	312
Gas: Average.....	379	420	393	377	396
Maximum.....	435	470	425	420	490
Minimum.....	270	365	351	318	315
Feed, lb. per hr.....	68	82	109	121	100
Charging time, hr.....	6.25	5.5	4.5	5.5	24.0
Ammonia in products, per cent of total charged..	93.51	91.06	93.33	96.22	93.36
Extraction, per cent of available Al_2O_3	100.8	87.8	91.0	94.4	95.5
Mols $(\text{NH}_4)_2\text{SO}_4$ per mol Al_2O_3 in extract.....	0.76	0.67	0.77	1.08	0.62

gases passed through a coke-filled mist filter, the exhaust fan, a condensate trap, and finally a long discharge pipe, at which their volume and ammonia content were measured.

After the furnace had been brought up to temperature, the charge, consisting of approximately 33.3 per cent Utah County clay, 56.7 per cent ammonium sulphate, and 10 per cent water, was added at the rate of about 100 lb. per hour; the clay contained 30.0 per cent total Al_2O_3 and 25.0 per cent available Al_2O_3 , so that the charge contained 5.2 mols of ammonium sulphate per mol of available Al_2O_3 . The time required for the charge to pass through the furnace was approximately one hour.

At the end of each test a complete inventory was taken of the ammonia in the various products. The individual measurements involved in the ammonia balances are considered accurate to about 0.1 per cent. A summary of the important data on temperature, ammonia recovery, and

all tests except No. 5; only in test 5 was the ratio approximately 1, corresponding to ammonium alum.

Considerable difficulty was encountered in the early tests through sticking of the charge in the dropholes of the first two or three hearths. The sticking occurs when the temperature of the charge is in the neighborhood of 300°C. and is due to the formation of NH_4HSO_4 during the early stages of the baking reaction. The trouble was overcome by adjusting the temperature so that the sticking was confined to the second hearth, at which the dropholes could easily be reached for cleaning.

Leaching and Purification

The baked product is leached with sufficient hot water or cyclic mother and wash liquors to give a solution of ammonium alum that is saturated at about 70°C. The residue does not settle well, because of the tendency of clays to slime and because of the high specific gravity of the solution. Preliminary experiments, how-

ever, indicate that the alum can be crystallized in the presence of slimes in a manner similar to that employed in the Kalunite process.²³ The slimes can be removed much more easily from the relatively dilute and cool mother liquor than from the hot pregnant solution.

If the clay is baked with a deficiency of ammonium sulphate, some of the alum apparently is hydrolyzed to an insoluble

with part of the iron and titanium. In the crystallization step the titanium, lime, magnesium, silica, phosphorus, and ferrous iron in the pregnant solution show little or no tendency to go into the alum crystals, but appreciable amounts of sodium, potassium, and ferric iron are crystallized with the alum.

Some typical data on leaching and crystallization are shown in Table 6. These

TABLE 6.—Results of Ninth Cycle of Leaching and Crystallization Test

	Wt. or Vol.	Total Al ₂ O ₃	NH ₃	SO ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	CaO	MgO	SiO ₂
		Analyses, Per Cent									
	Grams										
Clay.....	100	30.1		0.4	2.43	0.40	1.13	0.60	0.40	0.70	48.4
Bake.....	155	15.3	5.58	40.5	2.57*	0.23	0.58	0.35	0.24	0.46	24.05
Leach residue.....	60	8.2	0.48	1.8	0.84	0.32	1.03	0.15	0.60	0.35	75.4
Crystals.....	212	11.3	3.65	35.8	0.004	<0.001	0.03	0.06	Nil	0.005	<0.001
		Analyses, Grams per Liter									
	Ml.										
Pregnant liquor.....	752	39.3	27.4	207.4	12.0	0.77	0.43	1.94	1.06	4.08	
Mother liquor.....	663	9.2	20.8	132.2	14.0	0.94	0.38	2.10	0.93	2.94	
		Extraction in Leaching the Bake, Per Cent									
Pregnant liquor.....		84.	97.4	98.8	90.2	58.	15.	87.	23.	77.	
		Distribution in Crystallization, Per Cent									
Pregnant liquor.....		100.	100.	100.	100.	100.	100.	100.	100.	100.	
Crystals.....		75.8	33.9	43.6	0.1	0.0	20.0	8.2	0.0	0.2	

* Considerable iron was picked up from the iron tube in which the clay was baked with ammonium sulphate.

basic sulphate when the baked product is leached with hot water, causing a slight decrease in extraction; the presence of a small amount of sulphuric acid prevents the hydrolysis. When a slight excess of the ammonium sulphate is used, the extraction in water is the same as in dilute sulphuric acid.

The amounts of various impurities dissolved in leaching vary widely, depending largely upon their mineralogical occurrence in the clay. Sodium, potassium, calcium, and magnesium in minerals such as feldspars and micas are not dissolved, but sodium or potassium in hydrated minerals such as alunite and magnesium in magnesite or dolomite are extracted, together

data were obtained in the ninth cycle of a series of cyclic leaches on Utah County clay, in which the iron was reduced by sulphur dioxide before crystallization and the mother liquor from crystallization was recirculated to the leach. The alum crystals were purified by two recrystallizations, and the recrystallization mother liquors, as well as the residue and crystal wash solutions, were advanced countercurrently. The clay contained 25.7 per cent available alumina, of which 96 per cent was extracted. The average NH₃ and SO₃ contents of the leach residues in the nine cycles were 0.30 and 1.6 per cent, respectively, corresponding to losses of 14.4 lb. of NH₃ and 94.4 lb. of H₂SO₄ per ton

of Al_2O_3 extracted; these losses can be decreased by more thorough washing. In two of the cycles, crystals containing less than 0.002 per cent Fe_2O_3 were obtained. Similar tests have been made in which the crystals produced were spectrographically free of iron and phosphorus and contained chemically undetectable amounts of lime, magnesium, silica, or titanium.

as 40 grams of Fe_2O_3 per liter. The iron and alumina can be precipitated in a readily filterable form by treating this liquor with ammonium carbonate; in this manner the iron can be eliminated with a loss of less than 3 per cent of the alumina extracted from the clay and with negligible loss of reagent.

If the SO_2 -reduction step is omitted

TABLE 7.—*Analyses of Ammonium Alum Produced on Pilot-plant Scale*

Batch	Analysis, Per Cent										
	Al_2O_3	Fe_2O_3	NH_3	SO_3	CaO	MgO	TiO_2	P_2O_5	Na_2O	K_2O	SiO_2
A	11.7	0.004	3.6	36.2	nil	nil	nil	nil	0.08	nil	0.008
B	11.7	0.004	3.6	36.2	nil	nil	nil	tr.	0.07	0.01	0.011
C	11.7	0.004	3.6	36.2	nil	nil	nil	tr.	0.06	0.02	0.012

In Table 7 are given the analyses of alum crystals produced in a similar manner on a semi-pilot-plant scale from approximately 1300 lb. of baked product accumulated from a number of preliminary tests in which various clays had been baked with ammonium sulphate in a small batch-type kiln. About 750 lb. of twice recrystallized alum was produced.

Elimination of Impurities

The impurities in the mother liquor, of which iron is the most important, gradually build up in the circuit as the solutions are recirculated. The impurities can be maintained below any desired level by bleeding off the proper proportion of mother liquor, from which most of the alumina, ammonia, and sulphate can be

virtually all the iron in the pregnant solution is in the ferric state. To determine the relation between the concentration of iron in the pregnant solution and that in the crystals, solutions of pure alum, saturated at 70°C. and containing known amounts of ferric ammonium alum, were crystallized at 20°C., with the results shown in Table 8.

Preliminary tests have shown that much of the iron can be eliminated from the circuit by treating the mother liquor or the pregnant liquor with clay calcined at 550° to 800°C. Although the proper conditions for this procedure have not yet been determined, the Fe_2O_3 content of the mother liquor was decreased in one test from 2.0 to 0.06 grams per liter, representing a removal of 97 per cent of the

TABLE 8.—*Effect of Ferric Iron Content of Alum Solutions on Iron Content of Crystals*

Fe_2O_3 in pregnant solution, grams per liter....	0.07	0.155	0.25	0.50	1.01	2.00	4.00
Fe_2O_3 in crystals, per cent.....	0.0008	0.0021	0.005	0.008	0.015	0.022	0.038

recovered by concentrating the solution by evaporation and producing a crop of impure secondary crystals to be returned to the leaching circuit. The impurities concentrate in the resultant secondary mother liquor, which contains as much

iron. In tests in which iron has been removed by adding calcined clay to the leach slurry, crystals containing as low as 0.006 per cent Fe_2O_3 have been produced without the use of sulphur dioxide and without recrystallization.

*Conversion of Ammonium Alum to
Aluminum Hydroxide*

The obvious method of recovering alumina from the ammonium alum is to precipitate it as aluminum hydroxide, using the ammonia evolved in the baking step. To those who have attempted to precipitate aluminum hydroxide by adding ammonia solutions to alum solutions, the difficulties involved are obvious; usually a gelatinous precipitate is formed, which is difficult to filter and wash.

Many methods for obtaining a satisfactory precipitate have been proposed²⁴⁻³² and virtually all of them were tried. Both ammonia and ammonium carbonate were studied as conversion reagents, since either might be produced, depending on whether indirect or direct firing were used during the bake. The methods investigated included treating alum solutions and alum crystals with ammoniacal solutions, with ammoniacal gases, and with solid ammonium carbonate. The strength of solutions, pressure of gases, temperature, and order of addition were varied. The best results were obtained by adding alum crystals to ammoniacal solutions. This method, which was first patented by Langlet and Rinman,²⁵ was therefore studied in further detail.

Precipitates with very good settling and filtering rates are produced when alum crystals are added to solutions containing an equivalent amount of ammonia, or preferably a slight excess, so that the final pH is approximately 7; if the pH drops appreciably below 7, even momentarily, the precipitates filter very slowly. The precipitates retain large amounts of water and sulphate.

Table 9 gives the results of tests in which 25-gram samples of sized alum crystals were dropped into ammonium hydroxide solutions containing ammonia stoichiometrically equivalent to the alum but varying in concentration; the precipitates were washed with 500 ml. of hot water.

TABLE 9.—*Effect of Crystal Size of Alum
and Strength of Ammonium Hydroxide
Solution on Precipitation of
Aluminum Hydroxide*

Alum Grain Size, Mesh	NH ₃ in Solution, Per Cent	Filter-cake Anal- ysis, Per Cent			SO ₃ after Ignition at 1000°C., Per Cent
		H ₂ O at 110°C.	NH ₃	SO ₃	
-28 + 65	25	66.4	0.03	1.9	<0.05
	15	69.5	0.02	1.4	<0.05
	10	74.0	0.0	1.1	<0.05
	5	74.0	0.0	1.0	<0.05
+65 + 100	25	66.0	0.03	2.3	<0.05
	15	74.7	0.05	1.4	<0.05
	10	77.5	0.05	1.1	<0.05
	5	73.7	0.02	1.0	<0.05
-100	25	80.8	0.08	3.7	0.25
	15	78.5	0.08	1.8	0.20
	10	79.0	0.05	1.2	0.20
	5	80.9	0.05	1.1	0.25

The data show that the precipitates, all of which settled and filtered well, retained 2 to 4 parts of water per part of aluminum hydroxide, the amount increasing as the size of the crystals and the strength of the solution decreased. The ammonia was washed out rather thoroughly, but large amounts of sulphate were retained, indicating that part of the alumina is precipitated as a basic sulphate. The amounts of NH₃ and SO₃ retained increased with increasing concentration of ammonia and with decreasing crystal size. The SO₃ was virtually completely eliminated by calcining at 1000°C., except when very fine alum crystals were used.

No satisfactory method has yet been found for appreciably lowering the water or sulphate content of the precipitate. The moisture content is decreased only a few per cent by centrifuging the precipitate or by filtering it in a pressure filter. The sulphate content decreases very slowly on repeated washing, but the rate of removal is far too low to be practical.

A typical analysis of a well-washed filter cake is as follows: NH₃, 0.03 per cent; Na₂O, 0.08; K₂O, 0.01; SO₃, 1.15; Al₂O₃, 13.6. The soda and potash analyses are

equivalent to 0.6 per cent Na_2O and 0.07 per cent K_2O for calcined alumina. The NH_3 and SO_3 contents correspond to 4.4 lb. of ammonia and 207 lb. of sulphuric acid per ton of Al_2O_3 .

Production of Alumina

The aluminum hydroxide precipitate is calcined at about 1000°C . to produce alumina. The product, although probably of very fine crystal size, tends to form particles that retain the size and shape of the original alum crystals. A typical size distribution of calcined alumina produced from minus 14-mesh alum is shown in Table 10. As would be expected from the

crystals of which the analyses are given in Table 7; 150 lb. of each batch of the crystals was added to a solution of ammonium hydroxide in a Dorr thickener, and the washed and dried* precipitates were calcined on the floor of a large Globar furnace. Chemical analyses of the calcined alumina are given in Table 11.

The high sulphate content of the product shows that it was incompletely calcined. Comparison of the analyses of the alumina with those of the alum from which it was made indicates that considerable silica and iron were picked up in handling. Considering the limitations of the equipment used for calcining and the oppor-

TABLE 10.—*Size Distribution and Analysis of Alumina*

Size, Mesh	Weight, Per Cent	Size, Mesh	Weight, Per Cent
-14 + 28	5.6	-65 + 100	25.4
-28 + 35	10.1	-100 + 150	12.3
-35 + 48	22.4	-150 + 200	4.0
-48 + 65	23.0	-200	6.9

Analysis, Per Cent

	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SiO_2	P_2O_5	SO_3	TiO_2
Chemical.....	0.015	Nil	Nil	0.07	0.6	Nil	Nil	<0.05	Nil
Spectrographic.....	Nil		<0.01				Nil		Nil

TABLE 11.—*Chemical Analyses of Calcined Alumina Produced on Pilot-plant Scale*

Batch	Analysis, Per Cent								
	Fe_2O_3	SiO_2	TiO_2	SO_3	K_2O	Na_2O	CaO	MgO	P_2O_5
A	0.08	0.35	nil	2.6	nil	0.60	nil	nil	nil
B	0.044	0.15	nil	2.6	0.03	0.40	0.2	0.05	nil
C	0.06	0.40	nil	1.0	nil	0.57	nil	nil	tr.

method of formation, the alumina particles are porous and light. The bulk density of the minus 35-mesh portion of the sample, as determined by means of a Scott volumeter for measuring the bulk density of pigment powders, was 53 lb. per cubic foot. Its chemical and spectrographic analyses are listed in Table 10.

Some calcined alumina was prepared on a semi-pilot-plant scale from the alum

tunities for contamination, the purity of the alumina product is considered quite satisfactory.

Production of Aluminum Metal

To determine the suitability of the calcined alumina for the production of aluminum metal, 68 lb. was electrolyzed in a small cell, which was operated continuously for about a week at an average

current of 432 amp. and an average voltage of 11.2 volts; cryolite containing 0.043 per cent SiO_2 , 0.035 per cent Fe_2O_3 , and no TiO_2 was used as the electrolyte. The aluminum produced was tapped from the cell at intervals and cast into bars weighing about $2\frac{1}{2}$ lb. Analyses of two of the bars are given in Table 12.

TABLE 12.—*Analysis of Aluminum Produced from Clay*

Bar No.	Analysis, Per Cent						
	Fe	Si	Ti	Cu	Mn	Pb	Al (by dif.)
7	0.16	0.44	tr.	0.03	0.01	nil	99.36
8	0.18	0.27	tr.	0.01	0.01	nil	99.53

Particular attention was paid to the behavior of the alumina in the bath. The alumina dissolved readily, and the cell functioned smoothly during the entire operation. Tests had been made previously in the same cell with Bayer alumina, and the alumina made by the ammonium sulphate process was as satisfactory in every respect as the Bayer alumina (taking into consideration contamination during calcining).

HEAT REQUIREMENTS

The major heat-consuming steps in the process are: (1) the ammonium sulphate bake, (2) evaporation of the filtrate from precipitation of aluminum hydroxide for recovery of ammonium sulphate, and (3) drying and calcining of the precipitate. Direct experimental data are available for the heat requirements of the baking step; the heat requirements of the other two steps are estimated indirectly from other test data.

Ammonium Sulphate Bake

During the baking tests in the Herreshoff furnace sufficient data were taken to calculate the heat balance. The heat balance for a 4-hr. period in test 5 of Table 5,

following the first hour of charging after the furnace was operating smoothly and temperatures and gas rates had become constant, is summarized in Table 13. Because of the high ratio of surface area to volume in the experimental Herreshoff furnace and the additional large radiating surface provided by the six firing tubes, approximately half the heat supplied was lost by radiation, convection, and conduction. The heat losses from a large commercial furnace probably would not exceed 15 per cent. It is probable also that only a slight excess of ammonium sulphate would be needed. In Table 13 is also given a probable heat balance for a large commercial furnace, assuming a 10 per cent excess of ammonium sulphate and a 15 per cent radiation loss. The total heat required for a commercial furnace as determined in this manner is equivalent to 29,400,000 B.t.u. per ton of Al_2O_3 extracted.

TABLE 13.—*Heat Balance of Ammonium Sulphate Bake*

	Pilot-plant Test		Commercial Furnace	
	B.t.u.	Per Cent	B.t.u.	Per Cent
Heat input: net heat of natural gas.....	1,340,000	100.0	447,700	100.0
Heat output:				
In baked product	21,700	1.6	21,700	4.9
In outgoing gas..	312,000	23.3	104,300	23.3
Vaporization of water.....	49,800	3.7	49,800	11.1
Heat of reaction.	179,400	13.4	179,400	40.1
Sublimation of $(\text{NH}_4)_2\text{SO}_4$	74,500	5.6	25,400	5.6
Radiation, etc...	702,600	52.4	67,100	15.0
	1,340,000	100.0	447,700	100.0

Recovery of Ammonium Sulphate

The ammonium sulphate content of the filtrate from the aluminum hydroxide precipitation can be built up by recirculating part of the solution before evaporation and by using the strong wash solutions to absorb the ammonia given off in the baking step. There should be no difficulty, therefore, in maintaining an ammo-

nium sulphate concentration of at least 500 grams per liter in the solution to be evaporated. The heat required for evaporating such a solution, using triple-effect evaporation, is equivalent to about 7,000,000 B.t.u. per ton of alumina. Assuming 90 per cent as the efficiency of steam generation, this is equivalent to a total of about 8,000,000 B.t.u. per ton of alumina.

Drying and Calcination of Aluminum Hydroxide

The final precipitate will contain about 25 per cent aluminum hydroxide and 75 per cent free water. Assuming that the filter cake enters the drier at 20°C., the dried cake is discharged at 150°C. and the water vapor is driven off at 100°C., the theoretical heat required is approximately 10,800,000 B.t.u. Assuming that the dried cake enters the calcining furnace at 90°C., the temperature of the discharged calcine is 1100°C., and the water vapor leaves at 250°C., the theoretical heat required for the calcination is 3,000,000 B.t.u., making a total of 13,800,000 B.t.u. per ton of alumina exclusive of heat losses in the products of combustion and by radiation, conduction, and convection. Assuming an efficiency of 70 per cent for these operations, the heat required for drying and calcining the aluminum hydroxide is 20,000,000 B.t.u. per ton of alumina.

Total Heat Requirements

The probable heat requirements for an operating plant are summarized as follows: ammonium sulphate bake 30,000,000 B.t.u. per ton of alumina; recovery of ammonium sulphate, 8,000,000; drying and calcination of aluminum hydroxide, 20,000,000; other heat requirements, 12,000,000. The total heat required is thus 70,000,000 B.t.u. per ton of alumina. This is equivalent to 2.7 tons of 13,000 B.t.u. coal per ton of alumina.

The amount of heat required for the process is quite high but it compares favorably with that of other sulphate processes. Because of the unusually high heat of formation of aluminum sulphate, all sulphate processes require a large expenditure of heat.

CONCLUSIONS

From the investigation as carried on thus far, it may be concluded: (1) that alumina suitable for the production of high-purity aluminum metal can be produced from clays by the ammonium sulphate process; (2) the total amount of heat required by the process is approximately 70,000,000 B.t.u. per ton of alumina produced; and (3) the loss of ammonia in baking the clay with ammonium sulphate would not exceed 140 lb. per ton of alumina extracted. The more important phases of the problem remaining to be investigated or requiring further study are: (1) elimination of impurities from the circuit; (2) decreasing the water and sulphate content of the aluminum hydroxide precipitate; (3) determining settling and filtering data for specific clays; (4) investigation of the relative merits of direct and indirect firing in the ammonium sulphate bake; and (5) determination of over-all reagent consumption.

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The Kalunite Process

By ARTHUR FLEISCHER,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE Kalunite process† for the production of metal-grade alumina from alumina-containing ores is applicable, considered from a general point of view, to any aluminous raw material that can be converted to potassium alum or equivalent normal alum. This result of modern technology has been the subject of a continuous study and development since 1929, on a laboratory and test-plant scale, with initial emphasis on the utilization of alunite as the raw material. The research and developmental program was carried out by the Kalunite Company and its successor, Kalunite, Inc., an affiliate of the Olin Corporation of East Alton, Illinois. The process is now approaching the time for a major test in its history with the completion of construction of a plant having a capacity of 100 tons of alumina per day in Salt Lake City for the conversion of Marysvale, Utah, alunite ores to alumina and potassium sulphate. The Salt Lake Alumina Plant is a Defense Plant Corporation project.

PRODUCTION OF ALUMINUM

The known existence of alunite deposits, especially in the Marysvale district, furnished the motive for the original inquiry into the utilization of this raw material for aluminum production. The deposits in this

region were actively explored during World War I and utilized for the production of potassium sulphate, an essential fertilizer, of which a shortage of monumental proportions then existed. Up to the twentieth century—for alunite is a mineral with an ancient history—it was used in Europe and in China as a source of potassium alum. It never had been used successfully in this country as a source of oxide for reduction to metal. Although the known reserves of this ore, which undoubtedly will be greatly expanded with a commercial outlet for this ore, are recognized to be sufficient for only a part of the present-day needs of aluminum, it has a definite place in the aluminum industry. Academically it points the way for future raw materials.

The aluminum industry has undergone a remarkable growth in the past few years as a result of defense and war requirements. Its expansion in many ways has been beyond belief and prediction, both in volume and location. This wartime status of the industry has accelerated the consumption of bauxite to such an extent that a re-evaluation of the raw material reserves for the future peacetime industry and for eventual wartime reserves is seemingly of concern. The generally accepted picture of bauxite ore reserves in the United States, especially in raw material suitable for treatment by the Bayer process, focuses attention on other possible sources of raw material of metal-grade oxide. The perspective for the development of a suitable process may have changed in the interim since the original work by Kalunite, but the ultimate goal is the same.

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† Features covered by U. S. patents and patent applications.

It is a textbook fact that the production of aluminum of a satisfactory metallurgical grade from alumina in the Hall-Héroult electrolytic cell requires an oxide of high purity, in contrast to the usual practice with the base metals, where pyrometallurgy can be applied economically. Metal-grade alumina, commonly referred to as aluminum ore, bauxite ore concentrates, or alunite ore concentrates, carries specifi-

tated the use of chemical procedures, or, more familiarly perhaps, hydrometallurgical practice. The history of attempts to use gravity concentration methods represents a separate line of attack with little success to record to date. The chemical procedures can be indexed into two principal classes, the alkaline and the acid processes with a variety of subclassifications.

TABLE 1.—*Comparison of Composition of Typical Ores Treated in the Kalunite Pilot Plant with Bayer Grade Bauxite Ore*
ALL ANALYSES ON A DRY BASIS

Description of Ore	Alunite			Clay				Bauxite	
	Low Grade, Utah	Intermediate Grade, Utah	High Grade, Utah	Oregon	Washington	Oregon	Montana	High-silica, Arkansas	Bayer, Grade A
Al ₂ O ₃ , per cent of ore.....	23.43	26.80	37.26	28.52	31.58	33.18	39.19	50.92	55-62
SiO ₂	36.16	31.80	9.27	43.47	38.35	49.35	45.97	23.94	2-7
FesO ₄	0.45	1.72	0.88	10.18	6.03	0.89	0.43	1.40	3-8
TiO ₂	0.43	0.22	0.15	2.18	2.19	3.43	0.88	2.83	2-4
SO ₃	23.36	22.60	38.01						
SiO ₂ , per cent of Al ₂ O ₃	154	84	25	156	121	148	117	47	13
FesO ₄	2	6	2	36	19	3	1	3	15
TiO ₂	2	1	0.4	8	7	10	2	6	7

cations limiting the common impurities of iron oxide and silica to a maximum of 0.02 per cent of each, while titania is limited to about 0.005 per cent.

These impurities represent the common adjunctive constituents of alumina ores, which must be separated from the alumina. They are present in varying amounts in all the ores from which recovery of alumina by any process is contemplated. Some values are assembled in Table 1 for typical ores that have been tested in the studies of the Kalunite process. The values have been expressed also as percentages of the alumina, to give a ready comparison with the prewar standard for bauxite ores used in the established Bayer plants.

The table serves to illustrate the first objective of any alumina process; namely, to separate the alumina from the bulk of the impurities. In general, this has necessi-

In processes in which sulphuric acid or sulphates are encountered as the means for effecting the separation of alumina from the associated oxide impurities, the normal alums have been one of the favorite intermediates for the accomplishment of this separation. In practice, the choice has been limited so far to potassium or ammonium alum, both of which have favorable solubility characteristics. Studies in the Kalunite laboratory and pilot plant have demonstrated the advantages of alum for the practical separation of alumina from silica, iron oxide, and titania. The greater part of experimental effort was confined to potassium alum, the logical derivative in the treatment of alunite ores, since the latter contains all of the constituents of potassium alum, differing only in the proportions.

BEHAVIOR OF POTASSIUM ALUM

Potassium alum is a stable double salt of potassium and aluminum sulphates and has the empirical formula $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. It fuses in its water of crystallization when heated to $92^\circ C$. at a sufficiently rapid rate, under conditions precluding loss of water. There is some evidence that a lower hydrate, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 12H_2O$, is stable at temperatures above about $80^\circ C$. When normal potassium alum is dehydrated to the composition of this compound, it will no longer fuse in its water of crystallization. Upon raising the temperature of the partly dehydrated material to about 225° to $250^\circ C$., the remaining water is evaporated to yield anhydrous potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3$. When the drying is carefully performed, the anhydrous alum is obtained in grains that are pseudomorphs after alum crystals. On heating the anhydrous product to temperatures of 850° to $1000^\circ C$., dependent on time, the sulphur trioxide combined with alumina is evolved, finally yielding a mixture of alumina and potassium sulphate.

This sequence of dehydration and desulphation operations accomplished by the application of heat to potassium alum has been the general scheme for many of the processes proposed for the production of alumina from clays and alunite ores. In the extrapolation of the process from the laboratory to test-plant scale, mechanical handling difficulties were encountered, mainly due to the physical characteristics of the mixture of molten potassium alum with solid alum, and of the product at higher temperatures due to an unexpected side reaction, which escaped notice in the laboratory studies. The difficulties encountered in design of apparatus for continuous operation led to a revision and study of practical means for effecting the dehydration.

One of the proposals involved a partial dehydration at about 80° to remove at

least one half of the water of crystallization. A study of the engineering and economic features of this scheme led to the conclusion that it would require excessive investment for plant, as it involved the evaporation at low temperatures of somewhat over 200 tons of water per day for a 100-ton alumina plant. A revision led to the proposal of spray-drying molten alum or its solution to produce an anhydrous or almost completely dehydrated alum.

This process, involving the dehydration of potassium alum by spray drying and desulphation of the anhydrous product, was the subject of a test-plant program in 1929 under the direction of W. Murray Sanders.* This enterprise preceded the Kalunite process; the experimental difficulties encountered in this work led to the ultimate solution of the problem of treating potassium alum without the attendant mechanical handling troubles. The details are of sufficient interest to recite here; transposing a difficulty into an answer is a lesson deserving frequent repetition.

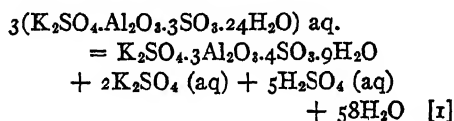
In the operation of the spray-drying apparatus, difficulty was experienced with the very small triplex pump used to pump the hot concentrated potassium alum solution to the atomizers in the spray drier and with plugging of the orifices of the atomizers. To avoid this vexing source of interruption, a monteju was set up and provided with means to keep the solution in it warm. The alum solution was transferred from the monteju to the atomizer by means of air pressure. It was presupposed at the time that an additional advantage of this system was the ability to maintain the temperature of the solution above the normal boiling temperature. However, no relief in the matter of plugging the orifices was found

* Mr. Sanders was well known to many members of the A.I.M.E., of which he was a member until his untimely death in 1931.

and a considerable amount of a white precipitate was found in the monteju.

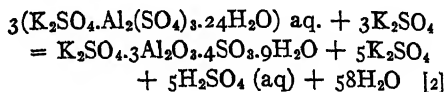
BASIC ALUM REACTION

Sanders made an experimental investigation of the behavior of potassium alum at elevated temperatures under pressure, to prove definitely that the precipitate was derived directly from potassium alum, and that it was not an accidental contamination due to impurities, either direct or indirect. When potassium alum solutions are heated under pressure, which is necessary to avoid evaporation and to raise the temperature sufficiently for the reaction to occur, hydrolysis occurs, causing the alumina to precipitate as a water-insoluble compound, similar in chemical composition to alunite. The reaction can be represented by the equation:



The basic alum* forms at a very slow rate when alum solutions are heated at the normal boiling temperature. From about 130° to 200°C. the percentage of alumina precipitated from a potassium alum increases linearly with the temperature to a yield of about 83 per cent of the alumina. There is no further increase in yield or percentage decomposition of the potassium alum at temperatures above 200°C. The precipitation of the alumina can be made practically complete at 200°C. by the addition of potassium

sulphate to the potassium alum in amounts equivalent to the potassium sulphate content, altering the equation to:



Equation 1 shows that in addition to the precipitation of alumina as a water-insoluble compound, sulphuric acid and potassium sulphate are regenerated in the solution. This illustrates an important requisite for all alumina processes; namely, the easy regeneration of the reagent chemicals. In the Bayer process, hydrolysis of the sodium aluminate solution produces aluminum hydroxide and caustic soda solution. The caustic soda solution, after separation from the aluminum hydroxide, is re-used for the treatment of bauxite. Losses in caustic soda, largely with the red mud, are made up by addition of caustic soda to the leach solution or by the addition of soda ash and lime.

The basic alum reaction—that is, the conversion of a normal alum into a water-insoluble basic alum with simultaneous regeneration of sulphuric acid—is the essence of the Kalunite process. It can be assigned the same importance in the technology of alumina processes utilizing alums as does the Bayer process for the separation of aluminum hydroxide from sodium aluminate solutions. Its importance was surmised and a preliminary laboratory survey of its formation and reactions, which was carried out early in 1930, impressed all sufficiently to carry on the project.

CALCINATION

The decision to turn to a study of basic alum as an intermediate in the alumina-manufacturing process was also indicated at the same time as desirable and feasible as a result of experiences with the calcination of anhydrous potassium alum. In the test plant, it was found that the anhydrous

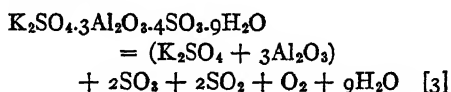
* Alunite and the synthetic precipitate from potassium alum described above have been termed basic alums in accordance with the usage designated by Mellor (*Comprehensive Chemistry*, 5, 352). Basic alum is a descriptive term indicating that the base alumina is present in excess over the stoichiometrical anion equivalent, exclusive of hydroxide ion. It does not mean that the compound is basic in the sense that it liberates hydroxyl ions to water. The naming of complex inorganic compounds in structurally descriptive terms is one of the modern problems of inorganic chemistry.

alum formed sticky masses in the rotary kiln, preventing a normal flow through the kiln. Examination of the mass indicated the formation of a potassium pyrosulphate, probably owing to a set of conditions under which the liberated sulphur trioxide was present at a sufficiently high concentration to react with the potassium sulphate, which is also liberated in the decomposition of the anhydrous alum. The unusual reaction is a sort of intramolecular rearrangement, but whatever the interpretation there is no doubt that this side reaction leads to a reaction mixture that is difficult to handle mechanically in a continuous operation. Observations of the characteristics of the calcine in the rotary kiln precluded any possibility that it might ever be handled in other types of furnaces, such as multiple-hearth furnaces with rabbling mechanism to move the calcine.

This reaction obtained on the calcination of potassium alum, which for convenience can be referred to as the pyrosulphate fusion, had been noted by other experimenters and numerous proposals had been made to overcome the pyrosulphate reaction. The physical chemistry of the reaction—that is, of the conditions under which it occurs—is still obscure. It is interesting to speculate on the subsequent history of the Kalunite project had the pyrosulphate reaction been thoroughly recognized, as it could have been by an adequate survey of the literature.

At any rate, the experience with calcination of potassium alum led to caution in the consideration of the calcination behavior of basic alum. It was found, however, that basic alum did not tend to form sticky masses. Laboratory tests were carried out using thick beds, from 2 to 4 in. deep, and with hand rabbles so that the calcination could be followed throughout the entire range of temperature. Laboratory studies showed that basic alum loses its water of crystallization continuously in the temperature range 200° to

600°C., in contrast to alunite, which starts to lose its water of crystallization at 450°C. Above 600° and to 900°, the sulphur trioxide combined with alumina is evolved. Later test work showed that it was desirable to raise the final temperature of calcination to 1000°C., thus diminishing the hygroscopic properties of the final alumina product. The over-all calcination reaction may be expressed by the following equation:



The solid product from the calcination of basic alum, derived from potassium alum, is a mixture of potassium sulphate and alumina, when the proper experimental conditions have been observed in effecting the operation. This mixture of alumina and potassium sulphate can be separated readily by treating with water or dilute potassium sulphate solution, thereby dissolving the potassium sulphate and leaving a residue of alumina. The alumina is separated from its suspension in potassium sulphate solution by thickening and filtration, preferably in a counter-current system. The alumina filter cake is dried at a low temperature to yield the final product. Potassium sulphate is recovered by evaporation or crystallization depending upon the dissolving circuit. The Salt Lake Alumina Plant has adopted a circuit using vacuum crystallization of the potassium sulphate.

RECAPITULATION

Recapitulating, the Sanders experimental program led to the development of the Kalunite process, of which the principal general features in the solution of the fundamental problem of the resolution of normal potassium alum into its components can be summarized as follows:

1. The conversion of potassium alum by heat-treatment under pressure to a

water-insoluble compound, a basic alum precipitate, with simultaneous regeneration of the solution of sulphuric acid and potassium sulphate.

2. The calcination of the basic alum precipitate to evolve as gases the water and sulphate, which is combined with alumina, to produce a calcine that is a mixture of potassium sulphate and alumina.

3. The separation of the calcine into its constituents, potassium sulphate and alumina.

The stoichiometry of this procedure was admirably adapted to alunite ore, since this ore contains one third of its alumina content in the form of aluminum sulphate. The sulphuric acid reagent required for a balanced operation could be recovered without the use of an acid plant for the conversion of sulphur dioxide, evolved in the calcination step, to sulphuric acid. This condition is not true if the ore is an aluminum silicate such as clay, for which means to recover the additional acid, above that regenerated in the autoclave reaction, must be provided to make the process self-sufficient in acid. Research on the application of the Kalunite process to clays has indicated means, other than calcination, for treatment of basic alum; the ultimate procedure will be mainly a matter of production costs.

PILOT-PLANT STUDIES

Although the first test started with the treatment of potassium alum in order to establish production on a larger scale and calcination of basic alum, the pilot-plant studies of the process have covered all phases from ore treatment to the final separation of alumina and potassium sulphate. At the start of the program, there seemed to be a dearth of experience and information to guide in the design of the various types of equipment indicated by the flowsheet. Progress was (and had to be) achieved in evolutionary, though not in homeopathic, jumps. In retrospect, it is

pretty clear that the operating experience gained throughout the development period was an essential component of the final perfection of the process.

DEVELOPMENT OF BASIC ALUM MANUFACTURE

The hydrolysis of potassium alum for the production of basic alum at elevated temperature and pressure requires the use of an autoclave (pressure vessel) constructed of materials that are resistant to the action of dilute sulphuric acid solutions. On a small scale, 50 to 100-gal. size, it was feasible to use externally heated lead-lined steel vessels. The first quantities of basic alum were prepared in such apparatus, but provided with means for rotating the entire pressure vessel. In translating this information to a continuous operation, an interesting difficulty was encountered. The rate of precipitation of basic alum is exceedingly high above 150°C., and the basic alum was precipitated as an adherent scale on the walls of the vessel, thereby seriously interfering with heat transfer to the flowing alum solution. On one occasion, the lead lining melted at one point underneath the scale.

This circumstance led to the development of the process of producing basic alum in an autoclave in which the temperature of the alum solution was raised to the desired reaction temperature by the direct injection of high-pressure steam. The steam condenses in the solution and raises the temperature by liberation of the latent heat of evaporation. The use of steam dilutes the solution, which is diminished by cooling the reaction mixture to the normal boiling temperature by blowing off steam from the reaction mixture in a blowdown tank. The suspension of basic alum in acid liquor was delivered to the blowdown tank from the autoclave through an orifice. Fig. 1 is a photograph of one of the pilot-plant installations of the auto-

clave and blowdown tank, which was successfully operated.

CALCINATION OF BASIC ALUM

In the early part of the development, it was considered essential, for economical

two bottom hearths were direct-fired. The two uppermost hearths were intended to be heated by the waste flue gases from the combustion of fuel in the intermediate four muffles. The four intermediate hearths were provided with sealing drop-

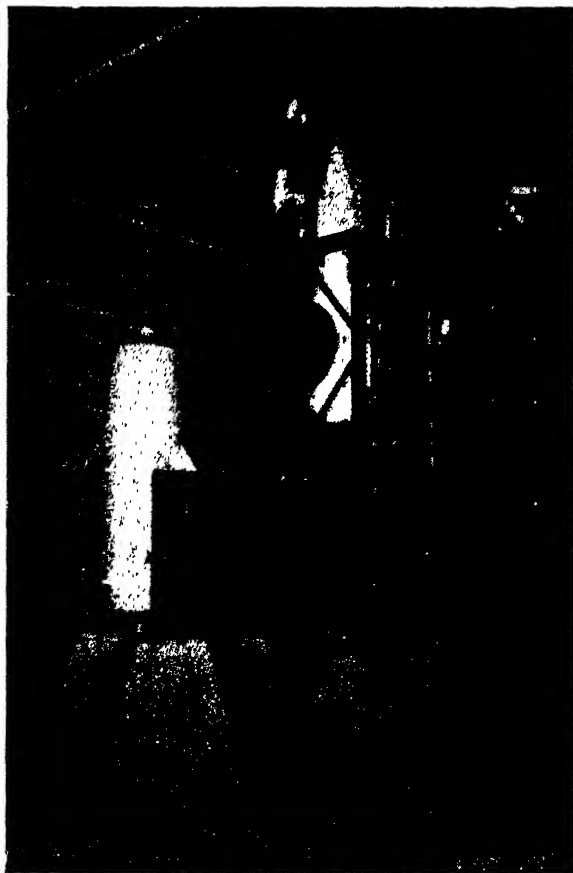


FIG. 1.—AUTOCLAVE AND BLOWDOWN TANK.

reasons, to recover all of the sulphuric acid content of the alunite ore. This thought, although modified with the passage of time, led to the installation of a multiple muffled-hearth furnace. This unit, shown in Fig. 2, was a 6-ft. i.d. furnace, with nine hearths, of which the uppermost was a drying and feed hearth. The next six hearths were muffled hearths of carborundum brick construction, while the

holes and separate flues for the collection of the sulphur oxide gas liberated in the calcination of the basic alum. It was intended to collect the bulk of the useful gas from the intermediate hearths and to use the two final hearths to eliminate the final traces of sulphate combined with alumina, as well as to raise the temperature to a point where the alumina is rendered substantially nonhygroscopic.

This operation led to the uncovering of one of the controversial questions on the Kalunite process, and in fact on all processes that in any way led to a possi-

ble of hydrogen sulphide in the gases from the direct-fired hearths.

When the calcine is in contact with carbon monoxide or unburned fuel at

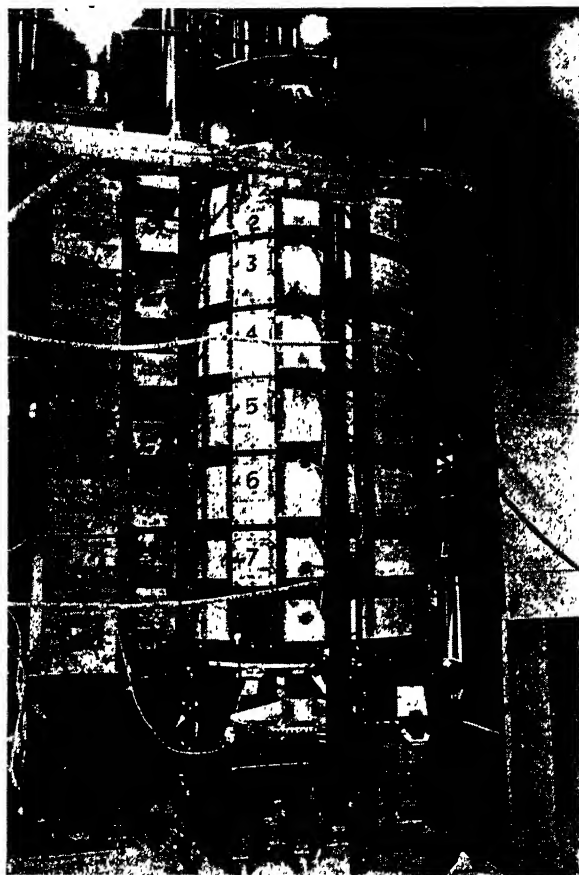


FIG. 2.—MULTIPLE MUFFLED-HEARTH FURNACE.

bility of potash contamination in the final oxide. In the laboratory, alumina had been produced with a potash content of the order of 0.2 per cent or less. The alumina residue from calcine produced in the pilot-plant furnace contained potash to the extent of 0.7 to 1.5 per cent. The clue to this condition was found in the presence of potassium hydroxide in the potassium sulphate liquors produced from the calcine, and in the occasional detection

high temperatures, it is possible to accelerate the high-temperature reaction occurring by the interaction of potassium sulphate and alumina to form a potassium aluminate. Under certain reducing conditions, all of the sulphate and part of the potash content can be volatilized. The potassium aluminate is only slowly soluble in water.

Metal-grade oxide produced from bauxite by the Bayer process usually contains

from 0.4 to 0.7 per cent soda (Na_2O) which cannot be removed by simple washing processes. The addition of this alkali to the electrolyte of the alumina-reduction cells usually requires a correction by the addition of aluminum fluoride. On a molecular equivalence basis, these limits for soda content can be translated to 0.6 to 1.0 per cent of potash. This amount of potash is considered by some aluminum technologists as intolerable in the operation of an aluminum cell, because of an inferred accelerated wear of the carbon cathodes caused by potassium ion in the molten cryolite baths in aluminum cells. The question of the effect of potassium on the cathode has not yet been answered effectively; tentatively Kalunite has set a limit of 0.2 per cent K_2O in metal-grade concentrates and this is expected to be achieved by complete muffling of the multiple-hearth furnaces and by proper control of the hearth atmosphere.

Elimination of aluminate formation in the calcination of basic alum is desirable for other reasons besides the contamination of the oxide with water-insoluble potash. When aluminate is formed, the slow hydrolysis in the potassium sulphate leaching circuit leads to the formation of a gelatinous coating on the bulk of the alumina, which tends to lower the settling and filtration rates of the alumina, and, in general, interferes with the proper elimination of the water-soluble potassium sulphate by washing.

DEHYDRATION OF ALUNITE

For the practical application of this process, alunite ore received considerable attention in the pilot-plant studies, mainly for the reason that an acid plant was not required in the treatment of this ore to produce potassium alum. The ores treated in the pilot plant varied in quality from 18 to 33 per cent alumina content. The pilot-plant test work indicated some variability in the behavior of ore from

different deposits, but mainly in the settling and filtering characteristics of the muddy potassium alum solutions produced from the ores. The difficulties encountered in the operation due to the muddy solutions led to important advances in the art of converting alunite and other ores to alum.

In the Kalunite process for alunite ore, the sulphuric acid is recovered as a dilute solution, at about 100 grams of H_2SO_4 per liter, which is in the range of concentration sufficient to produce about a 50 per cent potassium alum solution, a desirable concentration for a suitable water balance of the entire circuit. Alunite is insoluble in acid solutions of this concentration even when the ore is finely divided. The requirement for reactivity and solubility of an alunite ore in acid of the available strength is met by the dehydration of alunite at temperatures up to 600°C .

The object of the dehydration is to eliminate the bulk of the combined water without the loss of appreciable sulphur trioxide. The dehydration of alunite begins at about 450°C . and proceeds with an appreciable velocity at 550°C . The latter is evolved above 600°C ., and at an appreciable rate as sulphur dioxide at about 650°C . with concomitant loss of alumina solubility so that definite temperature limitations exist, creating the need for furnace-temperature control. Pilot-plant experience with rotary kilns and with multiple-hearth furnaces showed that the dehydration could be carried out with efficiencies of 90 per cent or over, based on the soluble alumina content of the dehydrated alunite and with the loss of less than 5 per cent of the sulphur trioxide content of the ore.

The important function of the dehydration procedure is to establish the solubility, and especially a high rate of solubility in dilute acid solutions. The elimination of the combined water—a correct expres-

sion, since it is probable on the basis of findings in the chemistry of alumina, which show that the water is present as hydroxide rather than water of crystallization—is termed a dehydration procedure, to avoid confusion in this process and especially in its presentation. The terms roasting and calcination, as applied to this step, often were interpreted to mean either that the sulphate content was eliminated or that the alunite ore contained sulphide sulphur, which was eliminated or converted to sulphate in the usual manner.

A secondary function of the dehydration procedure is to diminish the solubility of the iron content of the ore. The iron oxide in alunite ores from the Marysvale district is present usually in the form of accessory minerals and is definitely not a part of the alunite mineral content of the ore; for example, by isomorphous replacement of the alumina constituent. Since the ore is not soluble in dilute acids, it is not definitely known whether the dehydration has any effect at all on the silica portion of the ore. Silica is present as microcrystalline quartz in the so-called high-grade alunite ore from the vein deposits, while its exact form has not been identified in the low-grade replacement ore deposits. Even in the latter ores containing up to 40 per cent of silica in admixture with alunite, diffraction patterns and thin-section studies have not revealed any particular kind of silica.

EXTRACTION OF DEHYDRATED ALUNITE

The "metalunite"* is treated with a solution containing sulphuric acid and potassium sulphate in sufficient amount to convert the valuable constituents of the ore into potassium alum. The leaching circuit, which is a modified countercurrent treatment, is intended to operate to pro-

duce a 50 per cent alum solution; that is, one in which the solution portion of the pulp product of the leaching circuit is 50 per cent by weight of the compound $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ so that the total water content is about 75 per cent and the salt content, on the anhydrous basis, is about 25 per cent.

In the countercurrent treatment of metalunite, the final stage of the leaching, where fresh met meets the final solution, is intended to neutralize the free acid—i.e., uncombined acid—and it is advantageous to provide a certain excess of metalunite to lower the ferric iron concentration of the solution below 0.2 to 0.3 gram of ferric oxide per liter. At this range of iron concentrations, potassium alum has been found to crystallize from 50 per cent alum solutions, which are free of sulphuric acid, with an iron content below 0.002 per cent of Fe_2O_3 . The elimination of the free acid in the strong potassium alum solution is advantageous in the matter of iron elimination, since the amount of ferric iron crystallizing from solutions of given iron concentrations increases with the increasing free acid content of the alum solutions. It is also advantageous from the standpoint of the permissible alloys used in construction of the crystallizer circuit.

The rate of reaction of metalunite, especially when dehydrated completely without loss of sulphuric acid due to overheating, is extremely rapid. In a one-stage leaching of the metalunite, it is necessary to use a large excess of acid to accomplish complete extraction of the alumina content or to use a moderate excess of metalunite if a given volume of sulphuric acid solution of fixed concentration is to be neutralized. In either case the limit of the reaction is approached in about one-half hour at the boiling temperature. The rate of reaction of dehydrated clays is appreciably slower than for alunite ores.

* For convenience, dehydrated alunite has been named "metalunite," or "met," in keeping with the terminology on the dehydration of other solids, particularly kaolin and kaolinite.

CRYSTALLIZATION OF POTASSIUM ALUM

The 50 per cent potassium alum solution produced in the leaching circuit is permitted to settle in order to separate the bulk of the insoluble material that is advanced in the process to the acid circuit to extract the residual undissolved values. The muddy alum solution may be filtered before crystallization, to get a clear potassium alum solution, or may be cooled directly to crystallize potassium alum crystals in the presence of the insoluble material. In the test work on treatment of alunite ores it was soon found that the alum solutions produced from certain alunite ores were difficult to filter; that is, had low filtration rates when filtered in pressure filters such as the filter press or Kelly filter. In contrast, solutions derived from other ores, such as those from the White Horse deposit, were found to yield solutions that filtered at reasonable rates. The reasons for the differences in behavior have not yet been determined, although this matter is continually a subject of research and a challenge to thought. As a result of the difficulties encountered in the filtration of alum solutions from certain ores, research work based on certain observations in the pilot-plant operation led to the direct crystallization of pure alum crystals from muddy alum solutions under specified conditions. This new and distinct development by Kalunite offered some interesting advantages and was extended as a general treatment.

The solubility of potassium alum in water increases from about 10 per cent by weight at 20°C., to infinite solubility at 92°C., the fusion point of potassium alum. When a 50 per cent alum solution is cooled to 20°C., about 88 per cent of the alum content of the solution can be recovered as crystals; by the use of vacuum cooling an additional recovery is made, corresponding to evaporation of some of the solvent water. This means of recovery of alum from its solutions is one of the

advantages in using alum as an intermediate. The crystallization affords a separation of the alumina from the soluble impurities contained in the solution.

When the crystallization of alum takes place from a solution containing slime derived from the ore, conditions can be adjusted for the growth of crystals with little or no occlusion of the slime within the individual crystal grains. The separation of the slime and mother liquor from the alum crystals can be accomplished by filtration on a salt-type filter, using a coarse-mesh filter medium or by taking advantage of the difference in the settling rates of potassium alum crystals and of the slime in the mother liquor.

In the application of the mud crystallization process, the hot 50 per cent potassium alum solution is first admixed with potassium alum mother liquor in order to lower temperature and start crystallization. The mixture is then pumped into vacuum crystallizers, where heat removal and cooling is attained by boiling off water to a cooling water stream in a barometric condenser; the suspension of crystals and solution is further cooled in heat exchangers to between 20° and 30°C., depending on the temperature of the cooling water. The suspension of crystals and finely divided mud in potassium alum mother liquor is filtered directly on salt-type vacuum-drum filters. The crystals filter readily and can be washed on the filter to remove the bulk of the insoluble retained in the voids of the filter cake. Displacement of mother liquor from the crystals is particularly important, as contamination from this source may represent the largest percentage of impurities, especially of the soluble type. The mother liquor from the filtration is allowed to settle to separate the slime. The mother liquor is returned for re-use in the leaching circuit or after absorption of acid from the calcination of basic alum, and a portion is discarded to maintain impurities in the leaching and

crystallizing circuit at a maximum fixed concentration.

The alum crystals are dissolved before treatment in the autoclave. When the crystals are produced by the application of the mud crystallization process, the solution is clarified by pressure filtration to remove and ensure the absence of insoluble matter, which would contaminate the final alumina product. The clarification rates are very high in contrast to the filtration rates of the muddy alum solutions from the leaching circuit.

Summarizing, potassium alum of suitable quality for manufacture of basic alum and alumina may be produced from alunite ore by two Kalunite procedures using dilute sulphuric acid solutions recovered in the autoclave operation. The two procedures differ in the technique of handling the muddy potassium alum solution resulting from the reaction between a dehydrated alunite ore and the acid potassium sulphate solution. The steps are as follows:

1. Dehydration of alunite ore.
2. Countercurrent leaching with acid solution.
3. Decantation of muddy alum solution to remove bulk of insoluble matter.

A. Filtration Procedure

4. Pressure filtration and washing of filter cake.
5. Crystallization of clear alum solution.
6. Filtration of suspension to remove crystals, returning mother liquor to circuit.
7. Solution of crystals for autoclave treatment.

B. "Mud Crystallization" Procedure

- 4¹. Crystallization of muddy alum solution.
- 5¹. Filtration of suspension to remove crystals.
- 6¹. Settling of mother liquor to remove mud.
- 7¹. Resolution of crystals and pressure filtration of solution for autoclave treatment.

POTASSIUM ALUM FROM CLAY

Clay ores, especially those whose principal mineral constituents are kaolinite or halloysite, can be converted to potassium alum by a process similar to that employed for alunite ore. Like alunite, the alumina content of clays is insoluble in the dilute acid solution available from the autoclave operation, but becomes soluble after dehydration at temperatures above 450° and over a range to about 800°C. The optimum dehydration temperature varies with the characteristics of each individual clay.

In the application of the Kalunite process, as outlined for alunite ores, to the treatment of clay ores, there is one obvious difference, which has to do with the sulphuric acid balance. Clays do not contain any available sulphuric acid, so that it is necessary to recover the sulphur oxide gas produced in the calcination of basic alum by providing an acid plant to convert sulphur dioxide to sulphuric acid. This permits raising the concentration of the leach acid solution to a range between 150 and 200 grams of H_2SO_4 per liter. The increase in acid concentration is required to produce a 50 per cent potassium alum solution. It is also beneficial in increasing the rate of solution of the alumina content of the dehydrated clay.

The production of potassium alum from clay was the subject of a 16-months testing operation in the Kalunite pilot plant in Salt Lake City as a part of this country's alumina research program. Clays from the various known large deposits of the Northwest and one carload of high-silica bauxite from Arkansas were tested. The experimental work was a valuable and necessary prelude in advancing the application of basic alum technology for the utilization of clays as a source of alumina.

The pilot-plant operation on clays was limited deliberately to the use of the mud

crystallization process for the recovery of potassium alum from its solutions. It was found possible to extend the upper limits of mud concentration in the pregnant alum solutions. With solutions derived from alunite ores, the concentration of insoluble matter seldom exceeded 20 grams per liter. With the clay ores, it was found that a satisfactory grade of alum could be crystallized in the presence of mud at concentrations from 50 to 70 grams per liter, while with low-grade bauxite this limit was extended to as high as 100 grams per liter. Thus far, the Kalunite mud crystallization process appears to apply to all of the ores that are amenable to solution in sulphuric acid.

The work on clay in the pilot plant emphasized another important Kalunite contribution to the art of manufacturing alum from clays. In the countercurrent leaching process, the final neutralization of the solution requires the use of an excess of dehydrated ore in order to reduce reaction times to reasonable and allowable limits. This amount of ore is less than the total countercurrent feed required by the acid introduced at the tailings end of the circuit, leading to a split feed and a modified countercurrent system. The next point is to use only the coarse fractions of the dehydrated ore for the neutralization step, thereby eliminating losses of partially reacted, finely divided ore with the alum solution, the product of the leaching circuit representing the feed to the crystallizing circuit. The embodiment of these principles leads to a concurrent treatment of fines and a countercurrent treatment of coarse ore fractions.

The high-silica bauxite (23 per cent SiO_2) tested at the pilot plant was a disappointment in this type of circuit, owing to the tendency of the coarse fractions to break down almost completely into slimes. In recompense, the dehydration characteristics for high-silica bauxites were worked out with dehydration efficiencies of

over 90 per cent. The available information on the low-grade bauxites, presumably mixtures of kaolinite and gibbsite, indicated that dehydration diminished rather than increased alumina solubility. Such a decrease is true only for some conditions. For the dilute acid treatment, there exists an optimum combination of conditions for dehydration temperature, dehydration time, acid strength, and leaching period, for the maximum extraction of alumina.

The pilot-plant tests confirm the applicability of the process to clays for the production of alumina. The process, as described here, is capable of further important modifications, which, at the moment, appear to offer advantages in possible reductions in initial plant investment and in operating costs, factors that may be of lesser importance during the critical war period but which are bound to determine the ultimate course of the process in the postwar period. Research is planned to expand the available information and technical background for the proposed modifications, all of which involve the use of basic alum as an intermediate compound.

DISCUSSION

F. C. FRARY.*—I was very glad to hear Dr. Fleischer report that in plant practice the Kalunite process has produced alumina containing not over 0.1 per cent of K_2O . He was able to produce material of this grade in the laboratory many years ago, but the pilot-plant work produced alumina with many times that amount. While we have always felt it likely that such a low potash content could be produced in the plant, there has been no previous evidence to justify this belief. I think that Dr. Fleischer and his company are to be commended and congratulated upon the large amount of intelligent and careful work that has been put upon this process during the past 10 or 15 years. They appear to have done a very good job of investigating.

* Director, Aluminum Research Laboratories, New Kensington, Pa.

Magnesium from Potash Ores

BY LOUIS WARE,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

At the beginning of the present war, the United States faced the need to multiply its production of magnesium metal almost 100 times within the shortest possible period. Urgently needed for construction of military aircraft, incendiary bombs, and other war uses, magnesium was at the top of the list of critical war materials. Up to that time only one producer, employing only one process and using one raw material in a single plant, represented this country's entire production capacity. It was immediately desirable to plan a number of plants located strategically over the country and to expand an industry more rapidly and to a greater extent than ever before had been attempted in so short a time.

In 1939 this American producer, the Dow Chemical Co., was making about 7 million pounds of magnesium metal. It utilized as a raw material brine containing magnesium chloride, which was pumped from wells in Michigan. The logical approach to certain increased production was to employ the same process on the same raw material in other sections of the United States. In Europe and other countries, different processes had been used and different raw materials were being utilized, but all of the skill and knowledge for production in this country was that of using the Dow type of cell and magnesium chloride as a raw material. The Government was testing other processes, but none then had been proved commercially feasible.

DEVELOPMENT OF NEW PROCESS

The International Minerals and Chemical Corporation had available a large quantity of magnesium chloride at Carlsbad, New Mexico, contained in the end liquor produced from its potash plant since the building of the plant in 1941. It was the only company mining commercially a magnesium ore and having anything like this quantity of magnesium chloride liquor. The magnesium ore, langbeinite, was being mined from the 800-ft. level for its content of potassium sulphate. This ore, a potassium magnesium sulphate, was reacted in a base exchange plant with potassium chloride to produce potassium sulphate, the discharge liquor having a high content of magnesium chloride.

Three potash-producing companies are in the Carlsbad area, but only International has developed and is commercially producing the potash-magnesium ores. The lower, or No. 4, vein in that area is potassium chloride ore, and is continuous through all the properties. The langbeinite, or No. 2, vein is minable at the International property, but occurs sparsely, if at all, in other areas being mined in that vicinity.

It is understood that most of the magnesium produced by Germany comes from magnesium and magnesium-potassium ores obtained from potash mines.

It was logical for International to propose to make available this magnesium material and to offer its technical staff to design, construct and manage a magnesium plant for the account of the Government. The plan that finally was adopted by the

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War Production Board, Army Air Corps, and Defense Plant Corporation called for the invention of a process, design and construction of a plant, and the training of an operating crew that could remove the magnesium chloride from the end liquor of the potash plant as a dry, powdered cell feed (approximately $\text{MgCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$) and reject any impurities that would decrease the efficiency of the subsequent electrolytic processing. The Defense Plant Corporation, as owners of the plants, made available the electrolytic process and "know how" as used by the Dow Chemical Co. for the reduction of magnesium chloride in a molten cell bath and the attendant production of magnesium and hydrochloric acid. The large amount of electric power required was found available at the hydroelectric installation of the Lower Colorado River Authority near Austin, Texas. A block of 35,000 kw. was assigned to International's project by the War Production Board power pool, and the metal-reduction plant, with a rated capacity of 24,000,000 lb. per year, was built 8 miles north of Austin.

The production of hydrochloric acid from the electrolytic cells posed another problem, because it could not be wasted. A new process was developed, therefore, and a plant was designed and built at Austin to reclaim magnesium from dolomite rock, which is abundant in the Texas area near Austin. Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), after crushing, calcining and carbonation, is treated with hydrochloric acid to form additional magnesium chloride in solution. The solution is evaporated, impurities are removed and a magnesium chloride cell feed ($\text{MgCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$) produced in powder form. By this method of treating dolomite with hydrochloric acid, an internal balance is maintained in the plant, with only sufficient magnesium chloride from the Carlsbad cell-feed plant introduced to offset chlorine and chloride losses in the system.

INTERNATIONAL'S PRODUCTION METHOD

A brief summary of the method of producing magnesium used by International is as follows:

1. Magnesium chloride cell feed is produced from end liquors that contain magnesium chloride, at the Carlsbad, New Mexico, potash plant.

2. Magnesium chloride cell feed is processed in electrolytic cells at the metal-reduction plant at Austin, Texas, where magnesium metal and hydrochloric acid are made.

3. Additional magnesium chloride is produced in a cell-feed plant at Austin from dolomite, by treatment with this hydrochloric acid.

4. Magnesium metal is alloyed for use in aircraft, bombs, and fabricated parts.

Principal auxiliaries of the Austin plant are a hydrochloric acid plant for preparing 21 per cent HCl, rectifiers that transform alternating current to direct current, and natural gas for burning dolomite and heating the electrolytic cells.

The Austin plant began operations on Oct. 31, 1942, nine months after construction was started. During the first year of operation, the Austin plant produced 98 per cent of rated capacity, and at the end of its first year of operation is producing at 10 per cent over rated capacity. Recognition of the performance of the operating organization was given in the presentation of the Army-Navy "E" on Nov. 30, 1943.

The accompanying simplified flowsheet (Fig. 1) and the following description of the processes, as prepared by Dr. Paul D. V. Manning, Vice President in Charge of Research of the International Minerals and Chemical Corporation, give a picture of the problems met and solved in these magnesium plants.

"In the production of potassium sulphate, advantage is taken of the instability of langbeinite ($2\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4$) in contact with solutions at ordinary temperatures,

to contact it with an aqueous mother liquor from the final crystallization of the potassium sulphate. This decomposes the langbeinite and precipitates a mixture of

pletion and the solutions therefore contain some of each component.

"There remains the mother liquor, which is used to decompose more lang-

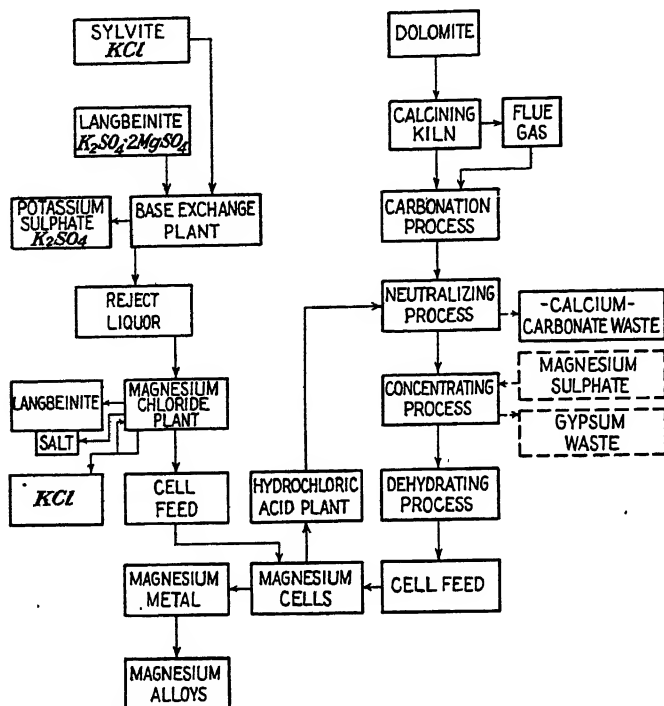
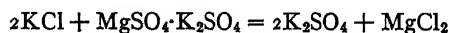


FIG. 1.—FLOWSHEET, INTERNATIONAL MINERALS AND CHEMICAL CORPORATION.

leonite (MgSO₄·K₂SO₄·4H₂O) and schoenite (MgSO₄·K₂SO₄·6H₂O) in the following reaction: $2(2\text{MgSO}_4\cdot\text{K}_2\text{SO}_4) + 10\text{H}_2\text{O} = \text{MgSO}_4\cdot\text{K}_2\text{SO}_4\cdot 6\text{H}_2\text{O} + \text{MgSO}_4\cdot\text{K}_2\text{SO}_4\cdot 4\text{H}_2\text{O}$.

"This mixture is separated from the solution by Bird continuous centrifugal filters, and the salt mixture is suspended in a saturated solution of potassium chloride, whereupon this base exchange reaction takes place:



The potassium sulphate is only slightly soluble; it crystallizes out of the solution and finally is removed by filtration and dried for sale.

"The above reactions do not go to com-

pletion. This mother liquor, after separation of the schoenite and leonite, is termed "reject liquor," and contains about 30 to 33 per cent of dissolved solids made up of sodium, potassium, magnesium, sulphate and chlorine ions. This solution, totaling about 500 tons per day, was formerly run to waste, but now forms the raw material for the production of magnesium chloride cell feed.

"Since a magnesium chloride containing under 0.2 per cent of sulphate as SO₄ is required, the process must first remove the latter. The total sulphate in the solid constituents of the brine amounts to approximately 26 per cent. Removal is effected by evaporation and reaction by carefully controlling concentrations and temperatures

to give a resultant solution stable in contact with langbeinite, but at a point where the solubility of langbeinite is at a minimum. The langbeinite therefore precipitates along with some sodium chloride and some potassium chloride. This salt mixture is separated out by a Bird continuous filter. This operation presents some problems because the temperature must not drop below the point of minimum solubility of langbeinite, or reach the point where langbeinite will decompose.

"Mother liquor from this separation, now practically free from sulphate and nearly free from sodium, then returns to the process, in which it is further evaporated.

"Through the addition of an exactly controlled amount of potassium chloride and exact control of temperatures and concentrations, carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$) is finally crystallized out in vacuum crystallizers. Potassium chloride, being nearly insoluble in concentrated solutions of magnesium chloride, the carnallite is leached with distilled water produced in the evaporation, which dissolves the magnesium chloride and only a very small amount of potassium chloride. There results a solution of magnesium chloride in which are suspended crystals of potassium chloride. These are removed by filtration, and the magnesium chloride solution now practically free from all other impurities except very small percentages of sodium and potassium chloride, is spray dried, and the powder is briquetted and shipped to Austin, Texas, to be fed into the magnesium cells."

SPECIAL PROBLEMS

Some of the difficulties encountered at Carlsbad, and how they were solved, are interesting. Because of the corrosive properties of magnesium chloride solutions it is considered impossible to utilize a triple effect evaporator commercially in concentrating solutions containing this salt. This is because the high boiling point rise of

magnesium chloride solutions makes it necessary to use so high an initial temperature that corrosion is very rapid, owing to formation of hydrochloric acid by hydrolysis of the magnesium chloride. This difficulty was overcome by lining the common steel bodies of the evaporators with acid-proof brick, backed with Pyroflex, and using Inconel tubes in the heaters. This type of construction proved quite satisfactory.

It is necessary to condense and save all the water removed from the brine. The condensates from the first two evaporator effects are returned to a sump for distilled water. Salinity indicators provide the needed controls. The vapor from the third effect is condensed by means of an S. and K. jet condenser, which draws its water supply from the distilled-water sump. The discharge is cooled by passing it through coils in the base of a cooling tower. Distilled water is also used for operating the vacuum crystallizers.

At the time the Carlsbad cell-feed plant was built, it was found that there would be an unexpected surplus of cell feed from the Dow sea-water processing plants at Freeport and Velasco, Texas. Temporary equipment and "hook-ups" made it possible to use magnesium hydroxide (MgOH_2) purchased from the Dow company as a slurry, transported in tank cars. This slurry was utilized to produce magnesium chloride, the initial and make-up chlorine being provided by purchase of hydrochloric acid and some magnesium chloride cell feed purchased from Dow. The shift to this temporary source of magnesium was directed by the controlling Government agencies, which then set back equipment for the Carlsbad cell-feed plant on the priority schedules. This delay, and orders to use some unsuitable substitute materials to ease the pressure on critical products, such as high-nickel alloys, caused delays and subsequent difficulties of operation. At present the cell-feed plant at Carlsbad is producing a cell feed of somewhat higher specifications

than those originally established, and it is being used satisfactorily for producing metal and chlorine. Freight of \$6.35 per ton on this cell feed shipped to Austin is a heavy item of expense, but because of the war requirements, it was necessary to take the raw material to the place where power was immediately available. Regardless of this expense, the Carlsbad cell feed can be delivered at a cost that compares favorably with that of cell feed from other sources.

In the magnesium metal plant at Austin, the gaseous effluent from the magnesium cells consists of a mixture of chlorine and hydrochloric acid. The hydrochloric acid is scrubbed out with water, the chlorine reacts with hydrogen from steam in a furnace to form hydrochloric acid, which also is removed by scrubbing. The resultant solution contains approximately 20 per cent of hydrochloric acid.

Dolomite from a quarry near Burnet, Texas, is calcined in a rotary kiln at Austin, a caustic burn being obtained. The resultant "dolime" is hydrated, and the hydrated slurry is selectively carbonated in a specially developed circuit. The calcium hydroxide alone is carbonated, so that there results a slurry of magnesium hydroxide and calcium carbonate suspended in water. The carbonation is effected by using the gases from the calcining kiln, compressed to 5 lb. by turbo-compressors. Part of the water is removed by means of Bird centrifugal filters and the cake is mixed with a solution of magnesium chloride from a point further on in the process.

This slurry then passes through a series of neutralizing tanks wherein the hydrochloric acid mentioned above is used to neutralize the magnesium hydroxide in such a manner that very little of the calcium carbonate takes part in the reactions. The carbonate is then removed by filtration and a part of the magnesium chloride is returned to use in mixing with the filter cake from the carbonation cycle. The remainder is concentrated by Ozark sub-

merged combustion evaporators. The small amount of calcium is precipitated by addition of magnesium sulphate.

After being concentrated to 34 per cent of magnesium chloride, the solution is cooled by a vacuum flash cooler to a temperature at which calcium sulphate is of minimum solubility. The liquid is then filtered to remove calcium sulphate and is concentrated in boiling kettles, flaked and dried in a shelf drier, from which it is ready for feeding to the magnesium cells. The cell feed produced at Carlsbad enters at this point.

Although both Carlsbad and Austin processes appear quite simple when viewed as abbreviated flowsheets, they depend upon accuracy of control of all variables. The Carlsbad process especially is one of complex applied phase-rule chemistry, depending for yield and purity of product upon exact control. Much of this has been worked out by means of automatic instruments, so that operation is not too difficult. Both processes are continuous.

Chlorine recovery averages more than 90 per cent, and good current efficiencies are being obtained.

Both of these processes have been brought into operation with very little time or opportunity for pilot-plant work, and surprisingly little difficulty has been encountered in production.

By production and shipment of additional cell feed from Carlsbad, it would be possible to produce hydrochloric acid for other purposes as a by-product at Austin. The setup is quite flexible when the two plants are operated together.

This enterprise has demonstrated the feasibility of recovering the entire ultimate value in products from ore mined in New Mexico from Government-owned land, the production of muriate of potash, sulphate of potash, magnesium metal and hydrochloric acid from the Carlsbad ores, leaving only the common salt and dirt from the ore as unused products.

The Basic Magnesium Enterprise

By C. J. P. BALL,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

PRIOR to 1939 the bulk of the magnesium metal produced outside of the United States was extracted directly from the ore and in the United States from magnesium chloride obtained as a by-product from the treatment of natural brines. A typical brine is one containing about 0.25 to 0.75 per cent bromine, 11 to 14 per cent sodium chloride, 9 to 11 per cent calcium chloride and 3 to 10 per cent magnesium chloride.

The state of Nevada was known to possess large deposits of magnesite ore (MgCO_3 , the carbonate of magnesium), in Gabbs Valley, near Luning, approximately 350 miles north of Boulder Dam. Deposits mined in Europe were supplying magnesite giving 97 per cent MgCO_3 with about 1 per cent each of silica, lime and oxides of iron and aluminum. Parts of the Luning deposits were almost equally rich, and the general average was of sufficiently high grade for production of magnesium. Power to the amount of 200,000 kw. was available immediately from Boulder Dam, and water from Lake Mead, and it was this combination of available power, water, and ore that led to the initial proposal to erect a magnesium reduction plant in southern Nevada to reduce the magnesite ores from Gabbs. The extraction of magnesium metal from these magnesite deposits had been considered by the I. G. Farbenindustrie of Germany as far back as 1929.

MINE AND OXIDE PLANT

The mine and oxide plant of Basic Magnesium Incorporated are perched upon the western slope of the Paradise Range, at an altitude of 5000 ft., overlooking the 30 mile desert panorama of Gabbs Valley, Nevada.

Ore Occurrence

The Gabbs magnesite ores occur in a thick series of flat, westerly dipping dolomites of Upper Triassic age. The magnesite bodies are exposed in steep canyon areas encircling the north and east edges of a northerly projecting tongue of a roughly elliptical stock of granodiorite, which intrudes the dolomite.

The magnesite mineralization is considered to be a replacement of calcium by magnesium through the agency of hydrothermal solutions associated with the intrusion of the granodiorite.

The ore bodies are of very irregular shape and distribution. Incomplete evidence points to deep pipelike replacement shapes that mushroom out erratically at various elevations. A wide latitude in the degree of magnesium replacement is reflected in a variance of quality from pure magnesite to magnesian dolomite.

The ore is a massive crystalline magnesite. Though some differences in characteristics occur between ore bodies, in general the ore is a medium-grained carbonate varying in color from white, through all shades of gray, to black. Recrystallized dolomite, which encloses and occurs as

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small masses within the magnesite, closely resembles the ore.

The magnesite ore contains varying amounts of the deleterious minerals—dolomite, calcareous crusts, serpentine, forsterite, talc, chlorite, pyrite and its oxide derivatives, as well as included dike-rock material. Those minerals occur in veinlets, joint fillings and coatings, interbedded layers, and irregular masses and disseminations in the carbonate. Their presence and mode of occurrence greatly affect the methods and details of mining operations.

Prospecting

The ore is blocked out by diamond drilling from surface. Outcroppings of ore, combined with geological mapping of the surface, indicate where sizable ore bodies may be expected and determine the beginning of a diamond-drilling program. Because of the extreme irregularity of the ore bodies, both horizontally and vertically, the present practice is to start drilling near the center of an ore body and work out to the boundaries at 100-ft. spacing. Data obtained from these holes determine the amount of interdrilling on 50-ft. centers required to block out the ore.

AX rods and 10-ft. core barrels are used. Cores are 1½-in. diameter and coring is started from the surface and continued throughout the depth of the hole. Core recovery varies from 76 to 98 per cent, the average over several months drilling being 93.1 per cent.

Mining System

All mining is done by open-pit methods, using 1½-yd. diesel-powered shovels loading into 10-cu. yd. diesel-powered dump trucks. High selective mining is required to maintain a grade of ore that can be handled by the mill to produce a good MgCO_3 product. A study of vertical cross sections through the ore bodies showing the information gained from diamond drilling

has made it possible to establish bench elevations to correspond with upper and lower limits of waste areas that lie generally in horizontal beds between beds of good grade ore. This planning of bench elevations has been the greatest aid to selective mining.

Ground is prepared for primary blasting by means of both wagon-mounted air drills and electric churn drills. All churn-drill holes are 9 in. in diameter. Both wagon-drill and churn-drill holes are loaded with free-flowing 65 per cent volume-strength dynamite and detonated with electric cap and Primacord.

The magnesite ore of this district has no special characteristics by which it can be visually differentiated from the surrounding dolomite. Because of this it is necessary to take an unusually high number of samples. All vertical wagon-drill and churn-drill blast-hole cuttings are sampled and the results are platted on bench assay maps. The ore and waste areas are thus known shortly after completion of drilling for any particular bench blast. The decision is then made concerning the manner in which the ground should be broken—that is, whether the waste and the ore should be blasted separately to prevent intermixing, or whether the entire shot area can be broken at one blast without mixing waste with ore.

Thus far in the history of this operation the quantity of waste handled in the pit in relation to ore delivered to the mill has been high, the ratio being approximately 1.4 tons of waste removed per ton of ore. This high ratio was necessary in order to make accessible for mining certain portions of the ore bodies that were covered with waste capping; also, the amount of waste that has had to be segregated from ore within the ore bodies proper has been considerable. However, improvements in metallurgy have been made from time to time whereby the mill has become able to handle a greater percentage of impurities

in the feed, thereby allowing the mine more latitude in the differentiation between ore and waste.

Crushing

Ore from mine is crushed to $5\frac{1}{2}$ in. in open circuit. The crushed ore discharges onto a 36-in. conveyor belt that elevates to vibrating screens, where a partial separation of fines is effected. The reject is varied from minus $\frac{1}{8}$ in. to minus $\frac{1}{2}$ in., depending upon the mine area being worked.

The products of screening after the fines have been removed are subjected to two stages of secondary crushing; first in standard and next in short-head cone crushers. The final stage reduces the ore to approximately $\frac{3}{8}$ -in. size.

Concentrating

The $\frac{3}{8}$ -in. ore is withdrawn continuously to four identical milling sections, each treating 500 tons per day. The description of one section is given.

A weight feeder controls the feed to the ball mill, which is $6\frac{1}{2}$ by 10-ft. grate-discharge type, operated in closed circuit with a 78-in. by 28-ft. spiral classifier. Mills are driven by synchronous motors through magnetic clutches. The grind is 72 per cent minus 200-mesh.

The classifier overflow at 30 per cent solids discharges by gravity to two 8 by 8-ft. conditioning tanks in series, whence it is pumped to the flotation machines. Several types of machines have been given a trial, with about equal results. A standard section consists of nine 42-in. subaerated cells, making a rougher concentrate and a final tailing. The rougher concentrate is cleaned in a six-cell bank of the same type, where a final concentrate is made and a cleaner tailing is sent to waste. Attempts to re-treat cleaner tailing by return to the rougher circuit have not thus far been successful.

Reagents are piped to central stations over the flotation machines from which

they are fed and distributed to the conditioners, to the pumps and occasionally to individual cells. The combination consists of varying amounts of aluminum sulphate, sodium pyrophosphate, caustic soda, starch, silicic acid, sodium silicate and naphthenic acids. Some of the quantities required are fairly large and a reagent mixing and storage plant larger than usually is provided for a 2000-ton mill is required.

The final concentrate from each section is pumped to two 54-in. by 33-ft. spiral classifiers, where the froth is diluted and the sands dewatered and fed to a 14 by 18-ft. internally fed rotary filter. The concentrate classifier overflows from all sections are combined and thickened in a 100-ft. thickener. The spigot is refloated in a nine-cell slime-cleaner machine, where a final slime concentrate is made and a slime tailing rejected to waste. The slime concentrate is thickened and distributed directly to the filters.

Tailings Disposal

The primary flotation tailings plus the cleaner and slime tails flow by gravity to four 54-in. by 33-ft. spiral classifiers, where the sands are discharged to the main tail race. The overflow is thickened in a second 100-ft. thickener for water recovery. The tailings dam is in a gulch $\frac{1}{2}$ mile to the north of the mill. Additional clear water recovered at the dam is pumped back to a sump that collects the overflow water from the three thickeners. From this point it is returned to a 150,000-gal. steady-head tank above the mill. Recovered water amounts to 1800 gal. per minute.

The fresh water requirement is 500 gal. per min., approximately half being used in milling.

Water Supply

The water supply comes from a series of eight wells in the valley below. Deep-well pumps deliver through 6-in. lines to a central station, where two high-lift pumps,

in parallel, lift 620 ft. through an 8-in. line to a 450,000-gal. storage above the plant. The pumping distance is 9200 ft. The mill-head tank is fed from this reserve, which is maintained for fire protection. All of the wells in use produce hot water, the temperature at the collecting station being 135°F. Pulp temperatures in the mill are 95°F. A cooling tower is provided for use if desired. In the present flotation treatment the use of hot water is an advantage.

Sampling and Analyzing

Sampling at all crucial points is automatic. Concentrate specifications are: insoluble, less than 1.0 per cent, R_2O_3 less than 0.50, and CaO less than 1.5. Maximum impurities in ore handled to date have been: 5.00 per cent insoluble, 3.00 per cent R_2O_3 and 6.10 per cent CaO. This lime content is roughly equivalent to 18 per cent dolomite in the ore; 5 per cent insoluble is equivalent to 7.5 per cent talc and serpentine.

Concentrate Drying and Storage

The cake from each filter discharges directly into a 7½ by 60-ft. rotary oil-fired drier. Cake moisture is 7 to 11 per cent and the drier discharge is substantially dry. The dried concentrate is conveyed to four storage bins from which it may be delivered either to trucks, for shipment to Las Vegas, or to the roasters.

Calcining

The 14-hearth roasters are 22 ft. in diameter. Arms and center shaft are air-cooled. Fuel-oil consumption is around 18,000 gal. per day. Fourteen burners are in use on the lower six hearths of each furnace, four having automatic temperature control and the other ten being manually adjusted. Brick-lined fireboxes built on the outside of the furnace ensure complete oil combustion before entering the high- CO_2 content furnace atmosphere. Maximum furnace temperature depends

upon the reactivity of calcine desired. The range is from 1300° to 1700°F.

The operating control is temperature. Recording instruments chart the temperature continuously on each hearth. The product is checked by shifts for initial and final setting time as determined by a Vicat needle on a Sorrel cement patty.

The calcine from each furnace discharges into a rotary water-cooled cooler, 5-ft. dia. by 45 ft. long, whence it passes to four concrete storage bins for loading into truck and shipment to Las Vegas.

Shipping

Haulage to the railroad at Luning is by means of specially designed diesel units consisting of a 32-wheel tractor, semitrailer and trailer. The net load is 25 to 30 tons. Truck bodies are completely enclosed, hopper bottom, and are filled through the top by means of flexible connections made to the scale hoppers. The hopper bottoms have dual cross screws and outside spline connections for power application in unloading. Discharge is through the center bottom of each hopper.

METAL REDUCTION PLANT

Basic Magnesium Incorporated's metal reduction plant is at Las Vegas, Nevada. The process used to extract the metal from the ore is the electrolytic reduction of magnesite developed initially by the I. G. Farbenindustrie of Germany, which has been operated extensively in England by Magnesium Elektron Limited of Manchester.

Early in 1941, Basic Refractories of Cleveland, which owned a number of magnesite mining claims at Gabbs Valley near Luning, Nevada, approached Magnesium Elektron Limited, proposing that the two companies cooperate in the design, erection and operation of a plant to extract magnesium metal from their Nevada ores.

Basic Refractories and Magnesium Elektron jointly created Basic Magnesium In-

corporated and as a result of this arrangement Magnesium Elektron then supplied Basic Magnesium Incorporated with the initial drawings, technical data, material and equipment specifications, and process flowsheets and details for a 5600-ton unit just completed in England, from which the B.M.I. reduction plant was mainly designed and built. M.E.L. loaned to B.M.I. its Chief Engineer, Chief Chemist and other members of its technical staff to advise, assist and cooperate in the erection program. With their assistance the entire layout at Las Vegas was designed by B.M.I. engineers to conform to conditions imposed by the size of the plant, the site and materials and equipment available in the U.S.A. Because of the urgent need for production, design and construction had to proceed simultaneously.

During the first six months of 1942, M.E.L. received at its plant in England 43 American members of the B.M.I. staff, and trained them to form the basis of the working organization required to operate the B.M.I. plant when built.

The foundation of the first metal unit was started toward the end of October 1941, and the first magnesium metal was poured from the cells on Aug. 31, 1942, ten months only from the date of the first excavation.

In October 1942, Basic Refractories' shares were acquired by the Anaconda Copper Mining Co., which then assumed responsibility for the management of Basic Magnesium Incorporated.

The total area of the Basic plant inside the fence is approximately 700 acres. Outside the fence are settling basins and effluent ponds, which consist of a series of dikes approximately 2 miles long. A town of some two thousand houses, and a trailer camp for one thousand trailers, has been erected close to the plant to provide homes for Basic's staff and work people.

To supply the Basic plant and townsite with water, a pipe line of 40-in. diameter was constructed from Lake Mead, 15 miles

away, lifting the water approximately 800 ft. from the surface of the lake to two 15,000,000-gal. reservoirs above and behind the plant. A pumping station of capacity of approximately 30,000,000 gal. per 24 hr. was constructed on the end of a cantilever bridge projecting over Lake Mead, which required more than 1000 tons of steel. The bridge anchor arm is more than 150 ft. long and the cantilever arm is 230 ft. long. To ensure supply during the lowest known drought, pump shafts were extended down 190 ft. from the end of the bridge. A water-treatment plant capable of handling 20,000,000 gal. per day was erected at the reservoirs.

Two transmission lines, one approximately 15 miles and the other 20 miles long, bring 200,000 kw. of electric power by widely separated routes from Boulder Dam to the plant. Three main substations at the plant, with a central control station and a control tunnel approximately 3400 ft. long, take care of the distribution.

B.M.I.'s requirements of chlorine are manufactured in a separate plant erected in consultation with the Hooker Electro-Chemical Co. and started up by this Company, which had previously trained at Niagara Falls members of the Basic Magnesium Incorporated staff to take over and operate the plant. The process used is the electrolysis of common salt, which produces approximately $1\frac{1}{8}$ tons of caustic soda for each ton of chlorine made. The chlorine plant at B.M.I. is one of the three largest in the world, producing 225 tons of chlorine and 250 tons of caustic soda per day.

The B.M.I. plant was designed to produce 112,000,000 lb. of magnesium per year, or approximately 153 tons per day. The plant has been running for a considerable period well in excess of this estimate.

The sequence of the process is shown in the accompanying flow diagram. The process makes use of anhydrous magnesium

chloride. It is a well established fact that the dehydration of magnesium chloride to the dihydrate ($\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$) can be accomplished without much risk of decomposi-

Process 3 does not permit of dehydration without decomposition and because of the difficulties of operation has not been employed on a large scale.

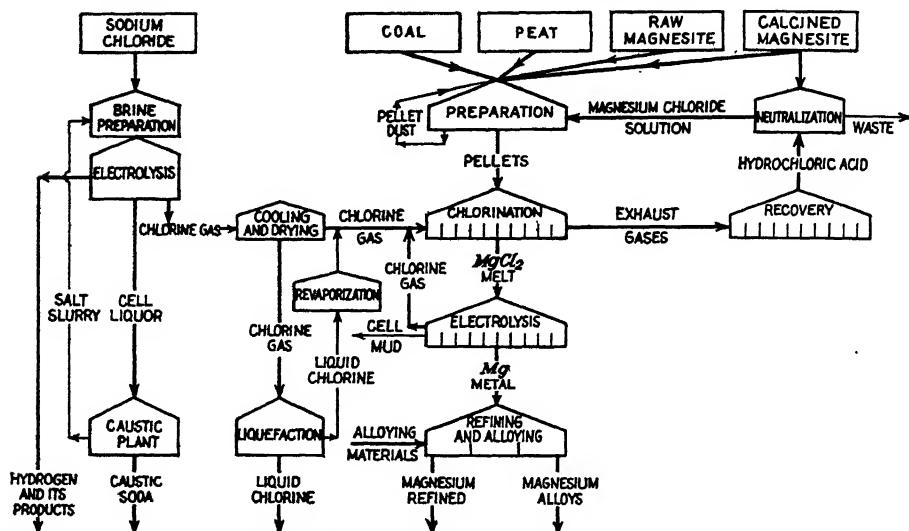


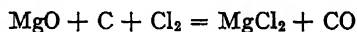
FIG. 1.—FLOW DIAGRAM, MAGNESIUM PLANT, LAS VEGAS, NEVADA.

tion. Successful dehydration beyond this stage without decomposition into hydrochloric acid and magnesium oxide is possible only if special practices are observed. Dehydration usually is carried out by one of three methods: (1) dehydration in the presence of dry hydrochloric acid gas, (2) dehydration in the presence of ammonium chloride, (3) dehydration by electrolysis in salt mixtures containing potassium chloride, and particularly in the impoverished electrolyte.

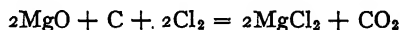
Process No. 1 does not yield a completely anhydrous magnesium chloride and the recovery and drying of the hydrochloric acid gas represents an appreciable charge both in operating and technical cost. This process is used mainly in cases where the brines contain valuable constituents, the extraction of which covers a considerable proportion of the cost of the process.

Method 2 has not progressed beyond the semitechnical scale.

The difficulties experienced in its attempts to produce a truly anhydrous magnesium chloride from hydrated compounds led the I. G. Farbenindustrie in 1924 to 1929 to study the reduction of magnesium oxide with carbon and chlorine in accordance with the known reactions



or



The I. G. Farbenindustrie successfully worked out and adopted a process using magnesite as the raw material, and this is the process worked in England by Magnesium Elektron Limited and at Las Vegas by Basic Magnesium Incorporated.

The magnesium carbonate used by B.M.I. at Las Vegas is supplied in the form of concentrates and calcine from its mines at Luning. The first stage in the reduction process consists of the preparation of the raw materials. The magnesite materials

in certain proportions are finely milled and then mixed with certain proportions of coal and of peat moss. The peat is added to give porosity to the pellets and to provide for the more rapid action of the chlorine upon the magnesium oxide content. Magnesium chloride solution made in the recovery and neutralization plant is added as a binder. The mix is then briquetted and dried, and coked in oil-heated rotary kilns.

The coked briquettes are fed into a shaft furnace or reaction tower lined with special refractory bricks and heated internally, using carbon resistors and electrodes. The solid charge rests upon a network of carbon blocks, which are heated by their resistance to the passage of three-phase alternating current. As the briquettes pass from top to bottom of the reaction tower or chlorinator, which operates at a temperature around $1000^{\circ}\text{C}.$, they meet a stream of chlorine rising from the bottom of the furnace. The carbon in the briquettes acts as a reducing agent and the magnesium oxide is converted to absolutely anhydrous magnesium chloride.

The fused chloride is tapped periodically from the bottom of the reaction tower and fed into special electrolytic cells. Chlorination and electrolysis take place in one building, in which, for the purpose of easy tapping and feeding to the cells, the chlorinators are lined up along one side of the cell room. The exhaust gases from the chlorinators are washed and the resultant hydrochloric acid solution is concentrated, clarified and neutralized with magnesium oxide, to provide the magnesium chloride solution used in the process.

Each unit contains eight chlorinators and 88 cells, the latter built in eight banks, each of eleven cells, with a capacity of 5600 tons p.a., the 10 units providing 56,000 tons p.a. The power conversion units are at the end of the cell rooms.

Electrolysis of the fused magnesium chloride is carried out in electrolytic cells

of special design, lined with refractory and insulating bricks to take care of the comparatively high working temperature.

The electrolyte consists of a salt mixture, which inhibits the natural tendency of anhydrous magnesium chloride to decompose when molten and which influences favorably the conductivity, viscosity and specific gravity of the electrolyte.

Provision of electrode surfaces of maximum area and the maintenance of a fixed ratio between the depth of immersion of electrodes and their distance are essential combinations of maximum economy.

The cells are designed to allow the separation and collection of the chlorine by use of ceramic curtain walls of high density and of particular properties forming a part of the cell and built in between the parallel electrodes.

Cast-steel cathodes and graphite anodes are used. The chlorine, which is quite dry and concentrated, collects in the anode compartment and is drawn off, filtered and recirculated to the chlorinators.

The cell is not externally heated, the electrical input of about 20,000 amp. being sufficient to maintain the temperature of the charge. The power consumption is approximately 9 kw-hr. per pound of metal. The magnesium metal collects at the cathode, floats to the surface of the melt, and is dipped out every 24 hours.

The removal of molten metal is effected by hand ladles and a fairly clean separation can be made between the metal and the fused chloride melt. Under normal operating conditions and with reasonable trained operators this should be more than 98 per cent pure.

This metal then passes to a refinery, where it is either refined for sale as pure metal 99.7 per cent or better or alloyed for sale as one of the constructional alloys in regular use.

In the refinery the metal is first melted in large cast-steel crucibles of 2-ton

capacity; during this process, Basic melting flux is used to minimize local oxidation. When the charge is molten, the alloying additions are made—aluminum and zinc directly and the manganese in the form of manganous chloride. The charge is then refined with a Basic refining flux, which is stirred into the melt, to carry down the suspended particles of chloride from the electrolysis metal, and to remove the remains of the melting flux. The refined metal is then superheated under cover of refining flux at a temperature above 850°C. for a period of 15 min. or longer, depending on the composition of the charge. The

charge is then cooled rapidly to 720° to 750°C. and poured either by a continuous ingoting machine or into 300-lb. crucibles for the casting of extrusion billets or rolling slabs.

ACKNOWLEDGMENTS

I wish to acknowledge the cooperation of Mr. T. C. Russell, General Superintendent, and Mr. C. P. Donohoe, Metallurgical Superintendent of the Gabbs operation, who supplied the information relative to the mining and concentrating operations used in the preparation of this paper.

Process Improvements at the Henderson Plant of Basic Magnesium, Incorporated

BY F. O. CASE* AND H. G. SATTERTHEWAITE,† MEMBERS A.I.M.E., J. R. COULTER‡ AND B. HARDEN,‡ MEMBER A.I.M.E.

DURING the two years that the Henderson plant has been in operation, a number of technical improvements have been made by the staff of Basic Magnesium, Inc., the effects of which were realized subsequent to the writing of the paper by Major C. J. P. Ball (p. 285, this volume).

PELLET MIX

The process as originally installed required the use of peat moss in the mixture going to the chlorinators. This had to be imported from Canada at a considerable cost, and, besides being expensive, constituted a serious fire hazard in the dry climate of Nevada. Experimentation looking toward its elimination had been going on for some time and was actively pushed as soon as operations commenced. It was found that a pellet mix containing no peat, which would chlorinate at a satisfactory rate, could be cast as a fluid slurry, which would set up into a hard mass having the desired porosity. For carrying out this operation, equipment similar to that used in the manufacture of phosphate fertilizer at Anaconda, Mont., was installed and proved eminently successful.

The dry materials, with peat moss and raw concentrates entirely eliminated, are mixed with magnesium chloride solution in two Pratt phosphate mixers and the resultant slurry is poured onto two 48-in. slowly moving rubber conveyor belts. By

the time the slurry has reached the head pulley, the material has set sufficiently to be broken and sized as desired.

The discharge from the casting belts is fed to the four rotary kilns in the preparation plant, where it is dried and coked to the proper degree for subsequent chlorination.

With the peatless feed the capacity of the kilns was found to be about double what it had been before, so that the four rotaries suffice for a 10-unit operation, thus making it unnecessary to operate the extruders and tunnel kilns.

In addition to saving the cost of the peat, the new system can be operated with about 85 per cent less labor than was formerly required in the preparation plant.

The new pellet production system has also made it feasible to install centralized crushing equipment with suitable conveyors and a loading station. Containers of 8000 lb. capacity were substituted for small cubicles of 1000 lb. capacity which formerly were used for charging the chlorinators, and trailer trucks were substituted for the small trains originally provided for transportation from the preparation plant to the chlorinators. These changes resulted in a considerable saving in handling and transportation charges.

HANDLING MOLTEN METAL

The molten magnesium originally was ladled from the electrolytic cells into small gas-fired brick-lined cars standing between the cell rows. From these cars the metal was poured into "cheeses" weighing from 150 to 300 lb. After solidification the

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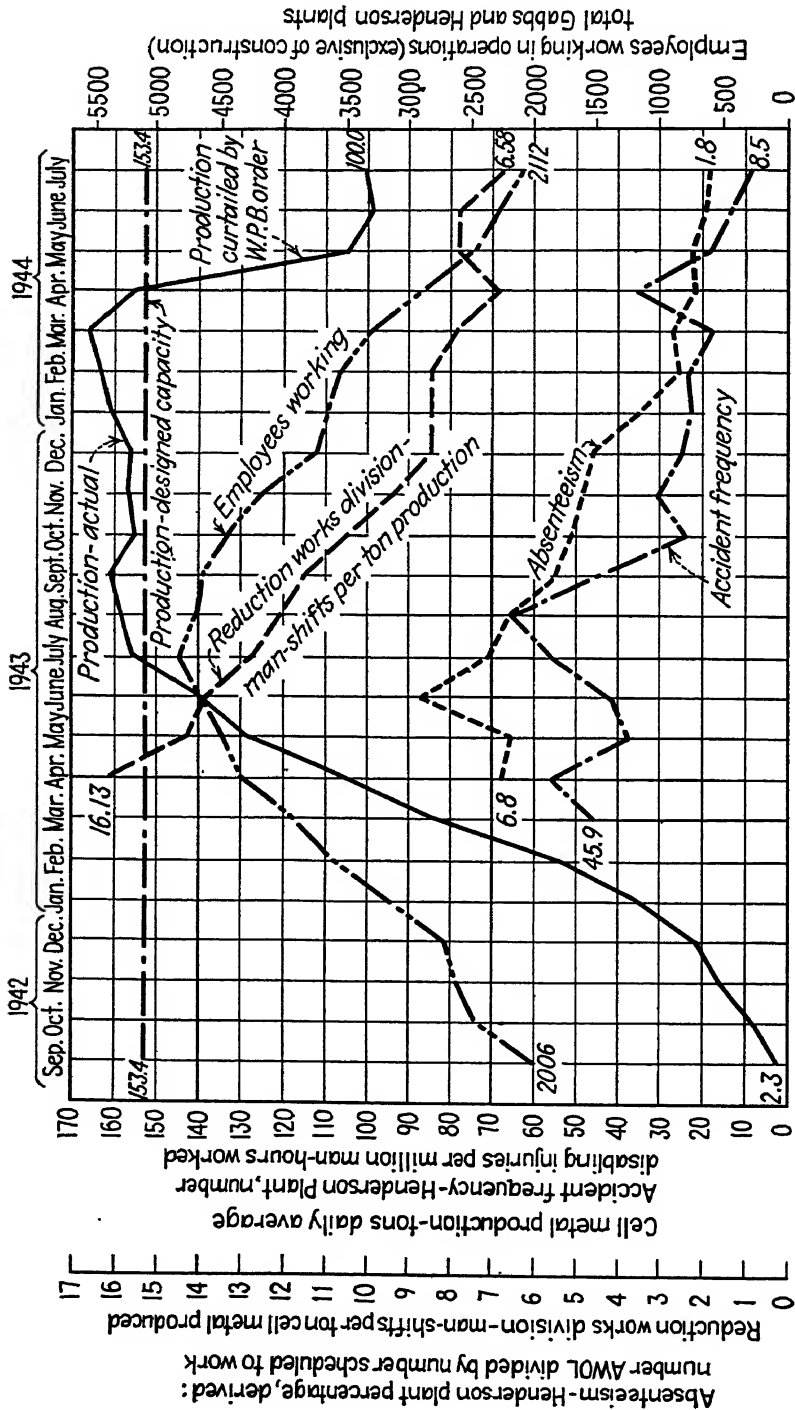


FIG. 1.—OPERATING ACCOMPLISHMENT, SEPTEMBER 1942 TO JULY 1944, BASIC MAGNESIUM INCORPORATED.

"cheeses" were hauled to the refinery, where they were remelted with considerable burning loss and appreciable fuel consumption. Now the metal is ladled from the electrolytic cells into specially designed pneumatic-tired, insulated cars of 4400 lb. capacity. When the car is full, any excess electrolyte that has been removed from the cell with the metal is pumped from the bottom of the car back into the cell.

The car full of molten metal is towed to the refinery and tipped by crane, so that the metal flows into the refining pot. This has led to a considerable improvement in working conditions as well as a saving in operating labor, fuel cost, burning loss and pot life. The refining can now be done with about half of the equipment originally provided for the purpose.

Additional substantial savings would result from the casting of 25-lb. notched ingots instead of the 5-lb. ingots that are now being made and wired into bundles of five. The casting machines originally were equipped with molds for casting the small ingots because it was anticipated that most of the metal from this plant would go to England, where the foundries are accustomed to using the small ingots, and prefer them.

AUTOMATIC CONTROL

In the electrical department, the substations supplying power to the various operations, including the electrolytic plants, were converted to automatic control, which reduced the number of electrical operators required from 84 to 17.

METALLURGICAL IMPROVEMENTS

Many other improvements in all phases of the operation have been made, and still are being made, attention at the moment centering primarily on improved metallurgical recovery. These investigations include the recovery of metallic magnesium from refinery dross, chlorinator debris, excess cell melt, cell mud, and so forth.

The Henderson plant was designed on the assumption that 1½ lb. of make-up chlorine would have to be produced in the Hooker chlorine plant per pound of metal produced. The actual consumption from the start of operations to the present time has been as follows:

Last four months of 1942.....	2.92
First six months of 1943.....	1.55
Last six months of 1943.....	1.18
First six months of 1944.....	0.95
Month of July 1944.....	0.64

Results obtained in the latter part of July indicate that the consumption of chlorine will be further reduced. The average for the first 18 days of August was 0.48 pounds.

In the Reduction Works Division, the trend of saving in labor is shown below:

Man-shifts per Ton of Cell Metal Produced

December 1942.....	26.1
April 1943.....	16.1
August 1943.....	12.1
December 1943.....	8.5
March 1944.....	7.8
July 1944.....	6.5

The figure for December 1942 does not mean much because only two units were in operation. It was not until the following summer that the plant was producing at capacity. On the other hand, July of 1944 was for a six-unit operation, as instructions had been issued in April to shut down four of the ten units because more magnesium was being produced than could be used.

SUMMARY OF PRODUCTION

The accompanying chart shows the performance of the plant from the time the first cells started to produce metal in September 1942 until the end of July 1944. It is to be noted that the production for each month from July 1943 until April 1944 inclusive was in excess of the rated capacity of the plant. The plant was built to produce 112,000,000 lb. of magnesium per year. A productive capacity at the rate of 120,000,000 lb. has been demonstrated.

Pilot-plant Production of Magnesia from Sloan Dolomite

By R. R. LLOYD,* MEMBER A.I.M.E., W. T. RAWLES,† AND R. G. KNICKERBOCKER,‡
MEMBER A.I.M.E.

(New York Meeting, February 1944)

IN July 1941, the Experiment Station of the Bureau of Mines at Boulder City, Nevada, began a study of methods of producing magnesium metal from magnesium oxide, with particular emphasis upon the direct use of magnesium oxide in a molten chloride electrolyte. The program was extended to include pilot-plant study of chemical methods for the preparation of pure magnesia from dolomites and magnesites.

Preliminary work on the production of magnesia from dolomite was done with the cooperation of Robert D. Pike and the Harbison-Walker Refractories Co. These investigations included a cooperative arrangement whereby the Bureau tested certain steps of the Harbison-Walker-Pike process. The process finally developed by the Bureau includes the precarbonation mixing step of the H.W.P. flowsheet prepared by Mr. Pike.

Two magnesium-reduction plants using MgO as a source of magnesium were being constructed in the West, and they enormously stimulated interest in various dolomite deposits as possible sources of the magnesia needed by them.

This paper describes one phase of this program—the operation of a pilot plant for producing cell-grade magnesia from dolomite from Sloan, Nevada.

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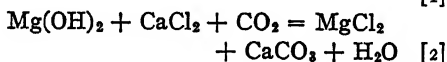
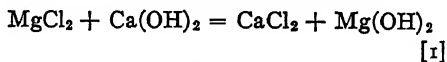
* Assistant Supervising Engineer, Bureau of Mines, Boulder City, Nevada.

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‡ Supervising Engineer, Bureau of Mines, Boulder City, Nevada.

PROCESS USED

The process developed for this purpose is an adaptation of a well-known process first proposed by Closson¹ and modified by others,²⁻⁴ involving the use of calcium chloride and carbon dioxide. It is based on the following chemical reactions:



The first reaction proceeds almost completely to the right because of the much greater solubility of calcium hydroxide as compared with magnesium hydroxide. Under equilibrium conditions, when only the four components shown in reaction 1 are involved, the ratio of magnesium to calcium in solution, according to solubility-product relationship, will be:

$$\frac{\text{Mg}^{++}}{\text{Ca}^{++}} = 3.3 \times 10^{-7}$$

This reaction is the basis of present commercial processes for recovering magnesium from sea water and dolomite.

The second reaction is, in effect, a reversal of the first reaction produced by adding CO₂. This reaction also proceeds nearly to completion, the solubility relationship being:

$$\frac{\text{Mg}^{++}}{\text{Ca}^{++}} = 2.1P \times 10^{-9}$$

where *P* indicates partial pressure of CO₂, in atmospheres.

¹ References are at the end of the paper.

The relationship of the two reactions is shown in the flowsheet, Fig. 1. Reaction 1 is effected in the magnesia circuit, producing a slurry of MgO and $\text{Mg}(\text{OH})_2$, and a solution containing CaCl_2 . Unreacted material, including siliceous impurities, is separated by a hydroclassifier, and the

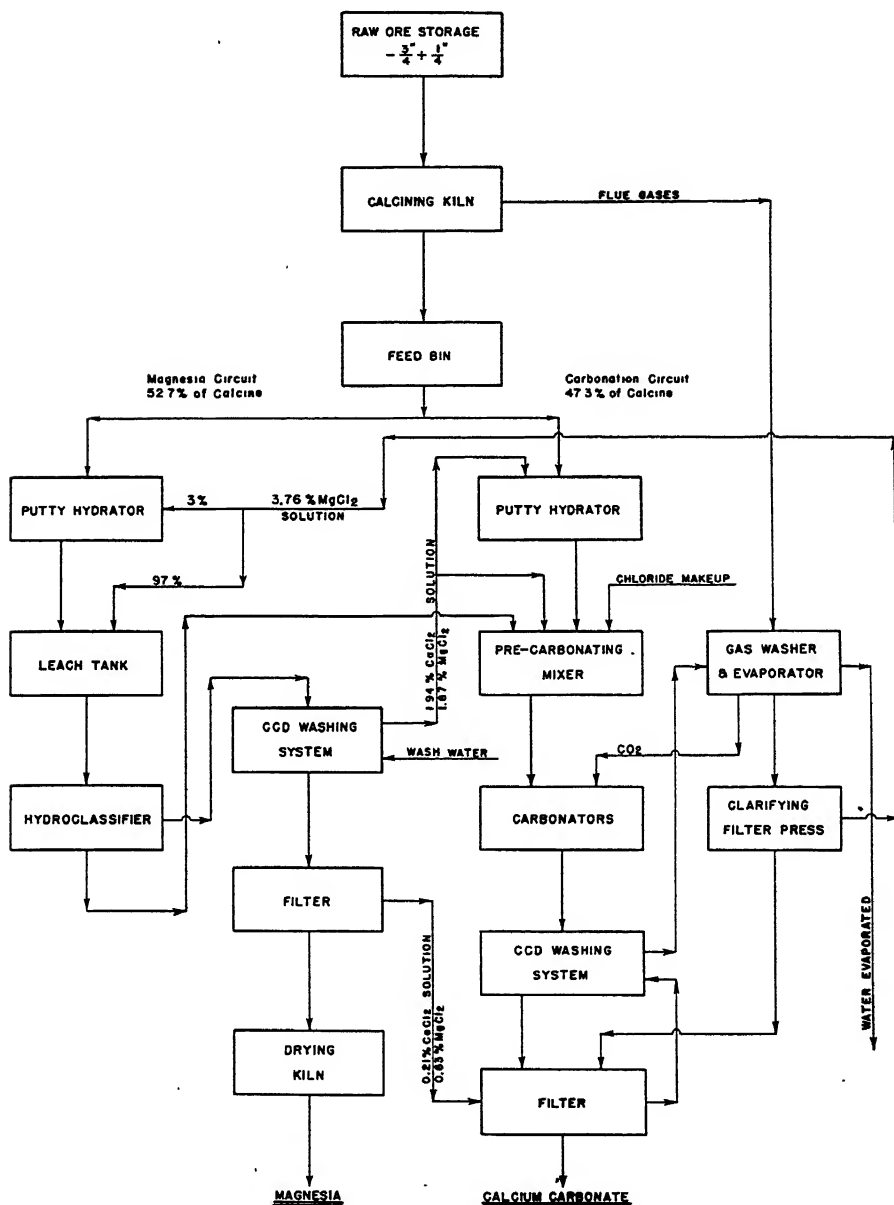


FIG. 1.—GENERAL FLOWSHEET.

is effected in the magnesia circuit, producing a slurry of MgO and $\text{Mg}(\text{OH})_2$, and a solution containing CaCl_2 . Unreacted ma-

terial, including siliceous impurities, is separated by a hydroclassifier, and the slurry is washed, filtered, and dried. Reaction 2 is effected in the carbonation circuit, regenerating the MgCl_2 and elim-

inating the calcium from both circuits as CaCO_3 . The CaCO_3 is washed and filtered.

easily washed, settled and filtered, and is sufficiently free of impurities for use in the production of magnesium metal. Much

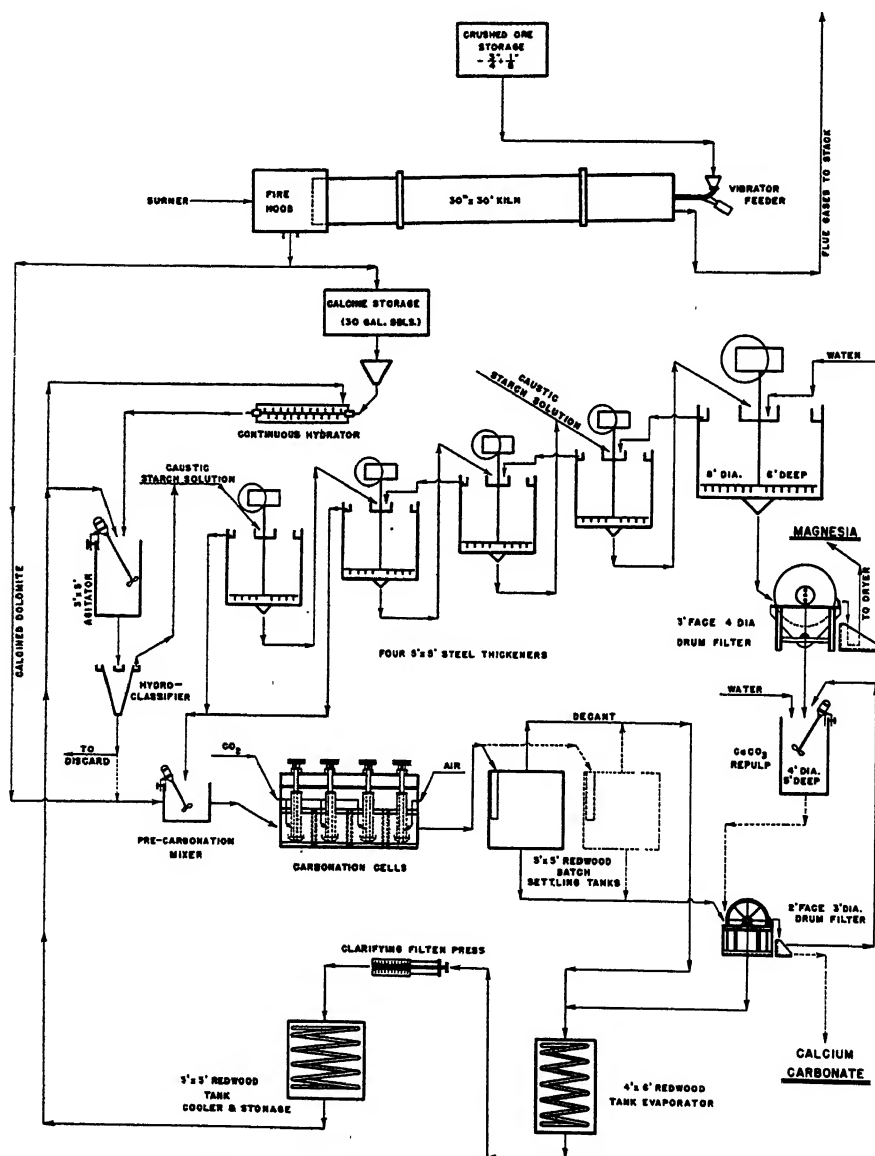


FIG. 2.—FLOWSHEET OF PILOT-PLANT EQUIPMENT.

The principal problem involved in successfully using this type of process is to obtain a magnesia precipitate that can be

attention has been devoted by various workers⁵⁻¹³ to avoiding the gelatinous mass of magnesium hydroxide normally

produced when the hydroxide is precipitated from magnesium chloride solutions by calcium hydroxide. Preliminary research indicated that the Sloan dolomites could be so calcined, hydrated and classified as to control the physical characteristics of the magnesia slurries, and emphasis was placed on continuous production of magnesia rather than on further exhaustive laboratory studies.

The pilot plant was operated continuously for 12 months, except for periods when plant alterations were being made. More than 40,000 lb. of magnesium oxide was produced, of which approximately two thirds was sufficiently pure to be used in the pilot electrolytic cell for the production of magnesium metal. The pilot-plant flowsheet and equipment used are shown in Fig. 2.

THE ORE

The dolomite employed in the pilot plant came from the Dawn and Bullion formations of the Sloan dolomite deposit, 19 miles south and west of Las Vegas, Nev. All dolomite and dolomitic hydrate used for the plant operation were contributed by the United States Lime Products Corporation from its commercial operations. The Sloan deposit contains 300 to 400 million tons of dolomite, uniformly high in grade.

A 21-yr. average of the dolomite mined is: CaO, 31.44 per cent; MgO, 21.04; SiO₂, 0.14; R₂O₃, 0.37. The dolomite obtained for pilot-plant work contained slightly less MgO than this average and averaged 0.10 per cent SiO₂. The rock is coarsely crystalline, a property that makes this material particularly applicable to the process used.

CALCINATION OF THE ORE

The temperature of calcination is a very important factor in determining the subsequent behavior of the calcine in the process. For the purpose of the magnesia

circuit of the flowsheet, the ore should be calcined at a relatively high temperature, not only to reduce the uncalcined CaCO₃ to a minimum but also to render the MgO relatively unreactive. The calcine, moreover, should be uniformly and freshly burned. During the early periods of plant operation, a commercially burned calcine was used exclusively. This material was calcined at 1100°C. in a 40-ft. vertical-shaft kiln. The dolomite was hand-picked and burned as large lumps, up to one foot in diameter. This calcine was entirely satisfactory for the carbonation circuit, and was used for this half of the flowsheet during most of the plant operations. It did not give consistent results in the magnesia circuit and the conclusion was reached that a more uniform calcine burned at a higher temperature would give better results.

Laboratory tests were made to determine the effect of calcination on the purity and settling rate of the magnesia slurries. Three typical results are shown in Table 1. The settling rates shown in the table are less than those obtained in the plant but they are in the same proportion.

TABLE 1.—*Effect of Calcination Temperature on Settling Rate and Calcium Removal*

Calcination Temperature, Deg. C.	CO ₂ in Calcine, Per Cent	Free Settling Rate, In. per Hr.	Purity of Product, CaO, Per Cent
1040	0.48	3.4	0.52
1150	0.46	3.9	0.18
1330	0.05	8.0	Nil

A 30-in. o.d. by 30-ft. rotary kiln was set up to continue the work. The kiln had a speed of $\frac{1}{8}$ r.p.m. and a slope of $\frac{3}{4}$ in. per foot. It was fed at the rate of 200 lb. per hour of minus $\frac{3}{4}$ -in. to plus $\frac{1}{8}$ -in. dolomite rock moistened with water. The average retention time was 2.5 hr. A satisfactory calcine was produced when the discharge temperature was 1300°C.

Several times during plant operations the temperature of calcination was reduced below 1300°C. and each time plant operation was so poor that the calcine was discarded. Recalcination at a higher temperature did not improve this material. The kiln temperature was limited to 1300°C. by the firebrick lining.

For use in the carbonation circuit, calcination at a lower temperature is desirable, both to increase the reactivity of the magnesium oxide in the calcine and to decrease the cost of operation. Laboratory calcination tests were made to determine the most satisfactory calcination temperature. The results are shown in Table 2.

Mg(OH)₂ and the unreacted MgO left from the dolomite are then washed and filtered together.

The degree of hydration of the MgO to give Mg(OH)₂ is a function of the hydration temperature. A low temperature of hydration is desirable so as to reduce the reaction of the MgO to a minimum; however, too low a temperature makes a coarse, granular hydrate that cannot be reacted effectively in the leach circuit. The optimum temperature of hydration varies greatly from one dolomite to another, and this factor can be determined only by experimentation. It was found that the MgO portion of the slurries hydrated slowly as it passed through the

TABLE 2.—*Effect of Calcination Temperature on Reactivity of Calcine for Carbonation Circuit**

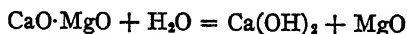
Calcination Temperature, Deg. C.	Original Solution, Grams per Liter		Carbonated Solution, Grams per Liter		Precipitation CaCO ₃ , Dry Basis, Per Cent		Remarks
	CaO	MgO	CaO	MgO	CaO	MgO	
725	14.17	10.27	15.70	13.98	44.10	21.42	Globar calcine. Very little reaction
950	14.17	10.27	0.28	28.16	59.75	2.20	Globar calcine
1040	14.17	10.27	4.16	20.11	54.50	2.77	Globar calcine
1055	14.17	10.27	3.98	21.94	55.15	1.40	Globar calcine. CO ₂ added slowly
1055	14.17	10.27	3.50	25.65	55.30	1.25	Globar calcine. CO ₂ added slowly
1300	14.17	10.27	3.08	22.44	54.35	2.97	Rotary-kiln calcine

* A slight excess of solution was used except at 950°C. That is the reason for the high (3 grams per liter) CaO in the carbonated solution.

It was decided from these tests that a kiln temperature of 950° to 1000°C. would be satisfactory for the calcine to go into the carbonation circuit.

MAGNESIA CIRCUIT, HYDRATION AND LEACHING

Calcium oxide hydrates rapidly in water with evolution of heat to form the hydroxide:



The calcium hydroxide produced by hydration reacts further with magnesium chloride brine in the leaching circuit to form insoluble magnesium hydroxide. The

washing circuit, but that once a satisfactory floc was obtained it tended to remain flocculated.

The first period of pilot-plant operation was from March 8 to May 8. Four methods of hydration were tried during this period, as follows:

1. Addition of freshly pulverized calcine to an excess of leach solution (cold hydration).
2. Grinding in a ball mill to "cream" the calcine.
3. Dry hydration with air classification to separate the uncalcined core (high-temperature hydration).
4. Strong agitation of the uncrushed calcine, $-\frac{3}{4}$ + $\frac{1}{8}$ -in., with a controlled

amount of water to yield a "creamy" slurry.

In each case the hydrated calcine was added to an excess of leach solution.

was fed to a small, batch-type, steel ball mill of 7-gal. capacity, rotating at 28 r.p.m., in batches of 8 to 12 lb. each. Solution was added for hydration at a ratio of 3 gal. of

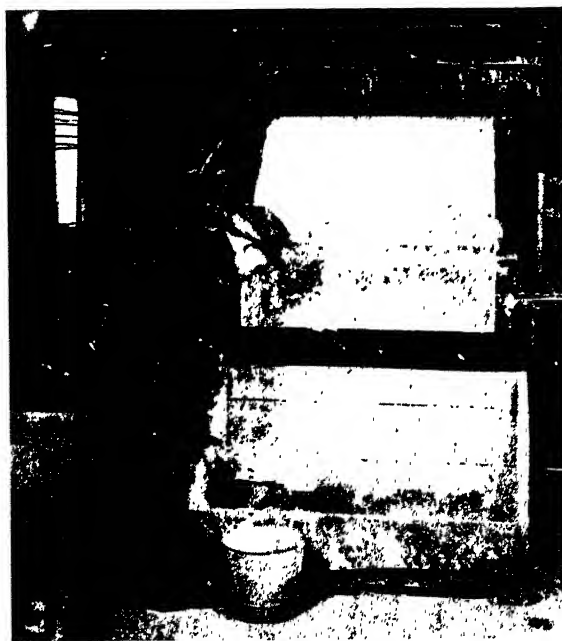


FIG. 3.—MAGNESIA FILTER.

Settling properties and average lime content of the washed residue for each method of operation are summarized in Table 3.

TABLE 3.—*Effect of Hydration Method on Settling Properties and Lime Extraction*

Method	Free Settling Rate, In. per Hr.	Compression Volume, Per Cent	Purity of Product, CaO, Per Cent
1	25	15	10
2	20	20	1.5
3	Very Slow	95	
4	20	20	1.0

Because of the poor results shown by Table 3, methods 1 and 3 were eliminated. Methods 2 and 4 were investigated further in the pilot plant.

During the period May 20 to Aug. 10, method 2 was used. The calcined dolomite

water to 10 lb. of calcine. The average analysis of the calcine used at this time was: CaO, 59.4 per cent; MgO, 38.8; CO₂, 0.2; R₂O₃, 0.6; acid insoluble, 0.2. The ball mill was rotated for one hour, the contents were removed and added to the leach tank, and the leach solution was added and mixed.

Method 4 was used from Aug. 10 to Oct. 28 and from Dec. 6 to March 5. The uncrushed calcine was vigorously agitated with solution to yield a "creamy" slurry. The same proportions of calcine and solution here used as for method 2. The batch hydrator consisted of a steel bucket, 1 ft. in diameter and 1½ ft. high. The mixture in the bucket was agitated for one hour with a ½-hp. portable mixer at 1750 r.p.m. The portable mixer had a 3-in., three-bladed propeller with a jagged

ole cut in the blades. The two methods are compared in Table 4.

TABLE 4.—*Comparison of Hydration in Ball Mill and Putty-type Hydrator*

Method	Settling Rate of MgO ^a	CaO in Final Product, Per Cent	Period
Ball mill....	Poor	6.88	July 7 to July 23
Ball mill....	Poor	6.00	Aug. 1 to Aug. 10
Mixer.....	Good	3.37	Aug. 16 to Aug. 26
Mixer.....	Good	2.88	Aug. 30 to Sept. 12

^a Exact average rates could not be determined on the thickeners. Comparisons were made from capacity of the entire system.

The ball-mill method of hydrating and grinding the calcine was discontinued because it reduced the magnesia slurry to such a fine state that it settled and thickened with difficulty, and it reduced the size of the insoluble impurities and unreacted material, making hydroclassification impossible.

longitudinally in the trough. Calcine was fed continuously at the rate of 10 to 15 lb. an hour at one end of the trough, along with leach solution at the rate of 3 to 4½ gal. per hour, and the hydrate overflowed the far end of the trough into the leach tank. This method gave good hydration and settling rates; however, because of the difficulty of feeding ¾-in. material continuously at the rate of 10 lb. per hour, there were variations in the hydration. These variations account for the high percentage of coarse material produced.

Another variation tried out in the pilot plant was the use of water as compared with leach solution for hydration. These experiments were made over a period of 3 days each on both continuous and batch hydration. The results are shown in Table 5. Table 5 shows that chloride brine for hydration gives the best settling rates.

TABLE 5.—*Effect of Method, Temperature, and Hydrating Solution on Composition of Hydroclassifier Overflow and Quantity of Underflow*

Hydration Method	Hydration Solution	Temperature, Deg. C.		Washed Classifier Overflow, Per Cent		Calcine in Classifier Underflow, Per Cent	Settling Rate
		Solution	Hydrate	CaO	MgO		
Continuous.....	Brine	44	63	0.54	99.45	24.7	Good
Continuous.....	Tap water	17	48	0.16	99.84	20.4	Poor
Batch.....	Brine	47	80	1.88	98.12	15.8	Good
Batch.....	Distilled water	62	85	10.63	89.37	7.5	Poor
Batch.....	Tap water	18	80	6.28	93.72	11.7	Poor

Screening and hydroclassification of the insoluble impurities and unreacted material were made possible when hydration method 4 was used, since these particles were much coarser than the magnesia slurry particles and therefore settled more rapidly.

A variation of method 4, employing continuous hydration in a standard putty-type hydrator, was used during the period Oct. 31 to Dec. 5. The hydrator consisted of a U-shaped trough, 6 ft. long and 8 in. wide. A shaft with rakes was rotated

For this reason brines were used thereafter for all hydration.

The thick hydrated material, made by any one of the methods described above, was then added to the leach tank. Leaching was done in a 200-gal. redwood tank, and the slurry was maintained in suspension by a ½-hp., 1750 r.p.m. portable mixer. The average residence time in the leach tank was 1.5 hr., when the calcine was batch-hydrated and 1.76 hr. for continuous hydration. The rate of flow from the leach tank to the hydroclassifier was 108 gal. per

hour. The temperature of the leach was maintained at 30°C. (room temperature) for the period up to Oct. 28. The temperature from Oct. 28 to Dec. 5 was maintained at 60°C. and from Dec. 6 to March 5, again at 40°C. Table 6 shows the importance of lower leach temperatures on the filtering rates.

TABLE 6.—*Effect of Temperature on Settling Rates and Filter Rates of Magnesia*

Temperature, Deg. C.	MgO in Thickener Underflow Thickener No. 3, Per Cent	Filter Rate, Lb. per Sq. Ft. per Day
30	8.9	127
40	8.1	100
60	7.0	70

Laboratory tests made to determine the optimum leach time are summarized in Table 7.

TABLE 7.—*Effect of Leaching Period on Settling Rate and Lime Extraction*

Leach Period, Hr.	Settling Rate, In. per Hr.	Purity of Product, CaO, Per Cent
1	0.5	3.5
1.5	7.0	2.0
2	5.0	1.9
4	3.0	1.9

These tests indicate that the optimum leaching period is 1½ hr. The purity of the product given in this table is not indicative of the purity of the product obtained during optimum plant operations but does indicate the effect of leach time on the purity of the product.

HYDROCLASSIFICATION

The Dawn and Bullion formations of the Sloan dolomites contain only a small percentage of siliceous impurities, and these are coarse-grained, being up to ½ in. in diameter. It was found that a large part of such impurities, along with particles of unburned and unreacted dolomite, could be separated from the

magnesia circuit by hydraulic classification. The particles so separated were examined chemically and microscopically and were found to consist of a wide variety of materials, including volcanic glass, andesite, altered igneous rocks, magnetite, hematite, unburned dolomite and unreacted calcine.

In the pilot plant, from the beginning of operations, a 17-mesh screen was placed over the leach tank. The primary use of the screen was to prevent the pipe lines following the leach tank from being plugged with coarse particles. The exact amount of material retained on the screen varied with the different methods of calcination and hydration. During smooth operation, when the hydration was correct and the calcine was reactive, the material amounted to 0.7 per cent of the calcine added to the magnesia circuit. A typical analysis of this residue is as follows: CaO, 36.0 per cent; MgO, 28.8; CO₂, 8.1; R₂O₃, 6.3; acid insoluble, 10.8. This material was discarded during normal operation of the plant.

The hydroclassifier, which was situated between the leach tank and thickener No. 1, consisted of a cone 18 in. in diameter at the top, 1¼ in. in diameter at the bottom, and 30 in. high, with a 2-in. launder. It appeared to be slightly large for the rate of flow and pulp density. An average of the underflow analyses for the optimum campaign is as follows: CaO, 19.1 per cent; MgO, 75.5; CO₂, 0.9; R₂O₃, 1.0; acid insoluble, 2.0. During this period the hydroclassifier underflow represented 11.3 per cent by weight of the calcine fed to the magnesia circuit. This could be cut down by using a slightly smaller hydroclassifier, but since this material was transferred to the carbonation circuit, the MgO present did not represent a loss.

The 19.1 per cent CaO in the hydroclassifier underflow was present as unreacted dolomite, and if it had not been removed by the hydroclassifier the magnesia produced by the process would

have contained an additional 3.0 per cent or more of CaO. It was for this purpose that the hydroclassifier was originally installed. The acid-insoluble residue re-



FIG. 4.—PILOT-PLANT CARBONATOR.

moved on the screen and by hydroclassification was approximately twice the insoluble residue indicated by the dolomite analysis. The discrepancy was caused by contamination from the kiln lining and sand, which blew into the circuit. In spite of this large removal, a small quantity of acid-insoluble residue was always present in the final product.

For purposes of process control, laboratory hydration and leaching experiments were made from time to time on different batches of calcine, and the slurry produced was screened to determine the size distribution. Although the size distribution obtained by screening was different from that obtained by hydroclassification, the screen served to determine the results that could be expected from the hydroclassifier.

A screen analysis of hydrates made from dolomite rock of the Dawn and Bullion

formations is shown in Table 8. The dolomites were calcined, hydrated, and leached in the usual manner. The leach residue was separated into a plus 100-mesh fraction and a minus 100-mesh fraction, washed, and analyzed. The results are summarized in Table 8.

TABLE 8.—Analysis of Sized Leach Residue PER CENT

Dolomite	Size, Mesh	CaO	MgO	CO ₂	Per Cent of Calcine
Dawn.....	+100	19.18	58.81	5.04	2.8
Dawn.....	-100	0.78	99.22		
Bullion.....	+100	32.74	49.39	3.60	2.5
Bullion.....	-100	0.80	99.20		

WASHING OF MAGNESIA SLURRIES

Following the leaching and hydroclassification steps, the material consisted of a solution containing calcium and magnesium chloride and a slurry of magnesium oxide and hydroxide. This magnesium oxide and hydroxide were separated from the soluble salts by continuous counter-current decantation.

Four 5 by 5-ft. thickeners and one 6 by 8-ft. thickener were used to wash the magnesia slurries. The larger 6 by 8-ft. thickener was used for the final washing stage to produce a pulp of maximum density for the filter. Owing to hydrolysis of the MgO in the slurry, as it passed through the circuit, the pulp density in the first 5-ft. thickener and in the final 8-ft. thickener was normally the same. A typical sequence of the MgO content of the slurries in the thickeners was 11.0 per cent, 9.5 per cent, 8.1 per cent, 7.3 per cent and 11.2 per cent, respectively. The thickener sizes should have been increased progressively to produce a pulp density of 11 to 12 per cent MgO in each underflow. This was not done in the pilot plant because the variety of thickener sizes required were not available.

Caustic starch was used as a flocculating agent. The usual concentration was 60 parts per million.

The washing efficiencies obtained agreed almost exactly with theoretical calculations, showing that there was no measurable tendency for the magnesia slurries to absorb the soluble salts.

The concentration of the original leach liquor was varied from 8 to 24 grams of magnesium oxide per liter. It was found that 14 to 18 grams per liter gave good washing results and still did not limit the capacity of the magnesia circuit. The limiting factors in plant capacity are the settling rate and compression volume of the magnesia slurries.

MAGNESIA FILTRATION AND DRYING

A drum filter, 4 ft. in diameter with a 3-ft. face, was used to filter the thickened magnesia slurry. Filtering rates varied from time to time, owing to experimental changes, but were satisfactory after the optimum calcination, hydration, and leaching techniques were determined.

A typical test showed a filter rate of 127 lb. of dry MgO per square foot of filter area per day. The drum speed was $\frac{1}{8}$ r.p.m. and the vacuum 20 in. of mercury. The filter cake contained 30 per cent MgO.

The filtrate was used to repulp the first calcium carbonate filter cake. It was not used for the magnesia wash circuit, because the CaCl_2 present tended to carbonate as it passed through the filter cloth.

The filter cake was repulped, drum-dried, and calcined in a direct-fired rotary kiln. Several commercial plants producing a similar product feed the filter cake directly to the kiln by mixing some return MgO dust with the cake. This method is preferable but was impractical for the pilot-plant work owing to intermittent operation of the kiln.

PURITY OF MAGNESIA

The calcium oxide content of the magnesia was gradually reduced as refinements were made in plant operation. The R_2O_3 and silica content was almost constant

after the hydroclassifier was installed. A summary of product analyses on several campaigns before the optimum campaign is shown in Table 9.

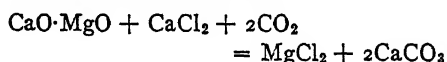
TABLE 9.—*Analyses of Magnesia Produced PER CENT*

Period of Operation	CaO	R_2O_3	SiO_2
May 2–Aug. 10.....	6.22		
Aug. 11–Sept. 15.....	2.90	0.39 ^a	0.01
Oct. 3–Oct. 28.....	2.70	0.40	0.08
Oct. 31–Dec. 5.....	1.56	0.40	0.07

^a $\text{Fe}_2\text{O}_3 = 0.36$, $\text{Al}_2\text{O}_3 = 0.03$.

CARBONATION CIRCUIT

The spent magnesia-circuit leach liquor was regenerated, as shown in Fig. 1, by adding more dolomite and reversing the reaction with carbon dioxide or flue gas from the calcining kilns. The effect of the carbonation reaction is:



Extensive experimental work was done on this reaction, since the first results obtained were unexplainably erratic. It was found that optimum results were obtained when all of the magnesia was present, before carbonation, as $\text{Mg}(\text{OH})_2$. Since optimum results were obtained in the magnesia leach by using an excess of MgCl_2 , the spent leach liquor contained appreciable MgCl_2 . This was converted to $\text{Mg}(\text{OH})_2$ by reaction with the hydrated dolomite before carbonation in the pre-carbonating mixer. The carbonation reaction was most satisfactory when there were approximately equal molar proportions of calcium chloride and magnesium chloride in the spent leach liquor.

Carbonation was carried out in the pilot plant by both batch and continuous methods. The apparatus used was a four-cell Denver Equipment Co. Sub-A flotation machine. It was modified for introduction of CO_2 and introduction and removal of slurries.

In batch work, each cell was filled with 50 gal. of spent leach solution and mixed with the desired amount of hydrated calcine, 9 to 14 lb. usually being sufficient. Carbonation continued until the pH dropped from 9.5 to 6.0, usually taking about 25 min. In continuous carbonation, the same quantities of materials were used and the pH was maintained at 9.5 in the beginning cell and 6.0 in the third cell. The fourth cell was used for aeration. The uniformity of results and higher settling and filter rates made continuous carbonation much more desirable. The normal filter rate when continuous carbonation was used was 1200 lb. of dry CaCO_3 per square foot of filter area per day.

Bottled carbon dioxide was used for the pilot-plant tests. However, several tests were made with mixtures of air and carbon dioxide to approximate flue gas. No difference was noted, except for lower absorption efficiencies.

The thickener overflow from the calcium carbonate circuit contained bicarbonate. This had to be removed because it caused precipitation of CaCO_3 with the magnesia when the solution was recycled to the magnesia leach circuit. During one period of operation, excess dolomitic calcine was used for this purpose. This reduced the calcium carbonate formation, but boiling was more effective. Since some evaporation is necessary in the circuit, and waste heat from the kilns would be available, it will probably be more convenient to decompose the bicarbonates by blowing hot gases through the solution.

OPTIMUM CAMPAIGN

The period from Dec. 6, 1942, to March 5, 1943, inclusive, was taken as the optimum and final campaign. During this period no flowsheet changes or equipment alterations were made. The operations were carried out exactly in accordance with Fig. 1, except for the washing and

filtering of the calcium carbonate. The hydroclassifier underflow was discarded.

A total of 97,440 lb. of dolomite was treated during this campaign, and 17,450 lb. of magnesia was produced. The operating data are tabulated in Table 10.

The plant operated smoothly, but at first the CaO content of the magnesia was unusually high and continued to increase. It was found that the dolomite contained considerable limestone, derived from the Crystal Pass limestone under the Dawn dolomite formation. The dolomite on hand was sorted to remove the limestone, and the CaO immediately dropped from a high of 3.6 per cent to 0.42 per cent.

TABLE 10.—*Pilot-plant Operation Data for Optimum Campaign*

Data taken directly from plant logs, lb. per hr.:	
Calcine used.....	30.00
	= 11.7 MgO
	17.9 CaO
Hydroclassifier underflow.....	0.21 CaO
	1.00 MgO
	(discarded)
Wash water for magnesia used.....	125.6
Magnesia produced.....	10.34 contained MgO
CO_2 consumed.....	16.60
CaCl_2 make-up (77-78 %).....	2.97
Wash water for CaCO_3	177.02*
Calculations based on plant data:	
MgO product recovered, per cent. . .	88.4
MgO accounted for (product plus hydroclassifier underflow), per cent	96.9
By-product CaCO_3 , lb. per hr.....	33.66
CO_2 carbonation efficiency, per cent.	98.2
Chloride loss (based on product analysis), lb. per hr.....	0.91
MgO lost in CaCO_3 , per cent.....	1.16
or, lb. per hr.....	0.39
Total water introduced, lb. per lb. MgO.....	18.8

* Included 111.5 lb. per hour of filtrate from the magnesia circuit.

Because of batch washing of the CaCO_3 , instead of countercurrent-decantation washing, a large amount of wash water was necessary to decrease losses of chloride. The loss of chloride with the calcium carbonate was still greater than it should have been.

WATER BALANCE

During plant operations the chloride loss varied inversely to the quantity of water evaporated. The plant was operated for six

months with no evaporation and for three months with a maximum evaporation of 13 lb. of water per pound of MgO. A balanced flowsheet, based upon recommended washing of the magnesia and countercurrent decantation washing of the calcium carbonate, shows that for each pound of magnesium oxide produced 8.05 lb. of water is added to the system. Of this quantity, 3.00 lb. is evaporated, 1.52 lb. is lost with the calcium carbonate cake, 2.35 lb. is present in the magnesia filter cake, and 1.18 lb. is discarded as weak liquor. The over-all chloride loss is 0.0344 lb. If the discarded weak liquor is evaporated, 4.18 lb. of water must be evaporated and the chloride loss is reduced to 0.0272 lb. per pound of MgO.

CONCLUSIONS

A pilot plant was operated for 12 months on Sloan dolomite, and the work was satisfactorily completed. The following conclusions were drawn:

1. Dolomite from the Sloan deposit can be treated successfully by this process to produce MgO.

2. A product analyzing 1.7 per cent CaO, 0.1 per cent acid-insoluble, and 0.4 per cent R_2O_3 can be readily produced. If a higher grade product is demanded, the calcium can be reduced to 0.5 per cent by more selective mining of the dolomite to prevent limestone contamination and by exercising sufficient control in the plant.

3. Dolomites vary considerably in physical and chemical characteristics, and experimental work is necessary to determine the adaptability of a particular deposit to this cyclic chloride process. It may be stated that, in general, dolomites with a coarse, crystalline structure can be readily beneficiated whereas those with an inherently finer particle size are considerably more difficult to treat. However, the hydroclassification step makes it possible to hydrate the finer grained calcines at a low temperature so that the slurries are not gelatinous and still remove unreacted material from the magnesia circuit.

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Production of Magnesium by the Carbothermic Process at Permanente

By T. A. DUNGAN,* MEMBER A.I.M.E.

(Chicago Meeting, October 1943; New York Meeting, February 1944)

THE thermal processes for the production of metallic magnesium can be divided into two general classifications, the direct reduction of magnesia with carbon and the indirect reduction of compounds of magnesium by reducing agents that are themselves products of carbon reduction. The latter are so chosen as to cause reduction of magnesium compounds wherein only the magnesium is liberated in the vapor phase.

Reducing agents used are: calcium carbide, silicon carbide, silicon, aluminum, various silicides or combinations of calcium, aluminum, silicon in iron. All of these are products of highly endothermic reactions and, with the exception of scrap aluminum, can be produced in an open, submerged arc furnace; that is, the arc is covered only by the charge itself.

The more investment in energy required to prepare such a reducing agent, the less is the energy required in the subsequent step to reduce the magnesium compound to the metal. It is impossible, however, to avoid the laws of thermodynamics, no matter how much circumambulation is resorted to in the preparation of successively more powerful reducing agents. Since each such step carries forward its own inefficiencies, it appears evident that the ultimate status of such processes is dependent upon the development of by-products.

EARLY EXPERIMENTS IN DIRECT REDUCTION

The direct reduction of magnesium oxide by carbon has a decided appeal to both the scientist and the industrialist. The successful production of the carbothermic plant at Permanente is a significant fact in the substantiation of this concept. Like most developments, however, the history of carbon reduction of magnesia is not one of triumph after triumph, or immediate heady success to the investigators. It is understood that one of the early investigators conducted an experiment wherein he placed carbon and magnesia in one end of an evacuated tube and managed to heat this end to a temperature high enough that magnesia and carbon deposited at the other end of the tube. The charge, unreduced, appeared to have been completely transported from the hot to the cold end of the tube.

This raised doubt for some time as to whether magnesia could be reduced at all with carbon. It was correctly suspected, however, that the magnesia was in fact reduced and the resultant magnesium vapor and carbon monoxide reacted upon one another upon reduction in temperature to reform the starting ingredients. Attempts were then made to dilute the two vapors by passing a considerable stream of hydrogen through an arc furnace charged with magnesia and carbon. Thus by dilution of the products it was expected to obtain metallic magnesium. The results were positive and metallic magnesium was

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obtained, but in insufficient quantities to encourage development of such a process.

A subsequent experiment involving surface cooling rather than dilution was also tried. A rotary disk, internally cooled by circulation of water, was placed in front of the outlet port of a small single-phase arc furnace. The axis of the disk was offset from the port and scraper blades provided to remove the deposited metal and to provide continuous exposure of a clean cool surface to the vapors issuing from the furnace. This experiment also gave positive results but again the efficiency was far too low for practical considerations.

The next phase was the so-called Radenthin or Hansgiring process, which was developed by the Austro-American Magnesite Corporation in Radenthin, Austria. This process was based on the principle of shock-chilling the effluent furnace vapors by a stream of hydrogen gas. One unit of 3000 kw. size was built at Konan, Korea, and one at Swansea, Wales. Both of these were built before the large plant was erected at Permanente.

PERMANENTE PLANT

The plant at Permanente consists of four 6000-kw. reduction-furnace units and differs only in several details, but not in basic principle, from the earlier plants at Konan and Swansea.

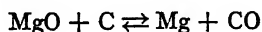
The shock-chilling medium used at Permanente is natural gas, which comes from the main lines that carry gas to the city of San Francisco from the Kettleman Hills oil fields in the San Joaquin Valley. The plant of the Permanente Metals Corporation was built south of San Francisco, in the foothills of the coast range mountains, solely because it was the site of the large cement plant operated by The Permanente Cement Corporation. The cement plant has a consumption of approximately 20 million cubic feet of gas for a 24-hr. day and it was thought that the use of natural gas as the shock-cooling agent

would make unnecessary the complicated auxiliary equipment required for the hydrogen quench.

The Permanente magnesium plant circulates to each reduction unit from a common system approximately 13,000 cu. ft. per min. of natural gas containing up to 6 per cent carbon monoxide. A continuous stream of freshly scrubbed and dehydrated make-up natural gas is introduced into the system in a ratio of approximately 20 to 80 per cent recycle. A corresponding amount (proportionally increased by the CO generated in the reduction furnace) is drawn from the system and pumped to the cement plant, where it is burned in the four 12-ft.-diameter, 465-ft. rotary cement kilns. This integration of gas usage with the cement plant eliminates the complicated auxiliary equipment required at the other plants for removal of the CO build-up from the hydrogen gas. The various processes for accomplishing this removal of CO from hydrogen would fill several papers far longer than this.

REDUCTION OF MAGNESIA BY CARBON

The basic principle of the process for the reduction of magnesia by carbon involves the reaction



which proceeds to the right at temperatures well above the boiling point of magnesium.

TABLE 1.—*Equilibrium Data on Reaction*
 $\text{MgO} + \text{C} \rightleftharpoons \text{Mg(g)} + \text{CO}$

$t^{\circ}\text{C}$	ΔF°	$P_{\text{Mg}} = P_{\text{CO}}$ (Atmospheres)
1300	38,260	2.20×10^{-2}
1400	31,250	9.10×10^{-2}
1500	24,270	3.19×10^{-1}
1600	17,320	9.75×10^{-1}
1700	10,400	2.66×10^{-1}
1800	3,510	6.53×10^{-1}
1851		1.0
1900	-3,360	1.48
2000	-10,200	3.09
2100	-17,020	6.08
2200	-23,810	11.27

Table 1 shows the equilibrium data taken from some recent calculations by K. K. Kelley, of the Bureau of Mines, which are considered the most accurate data regarding this reaction.

crystals are subsequently melted and alloyed in accordance with accepted magnesium foundry practice.

The raw materials used by Permanente are dolomite, sea water and petroleum coke.

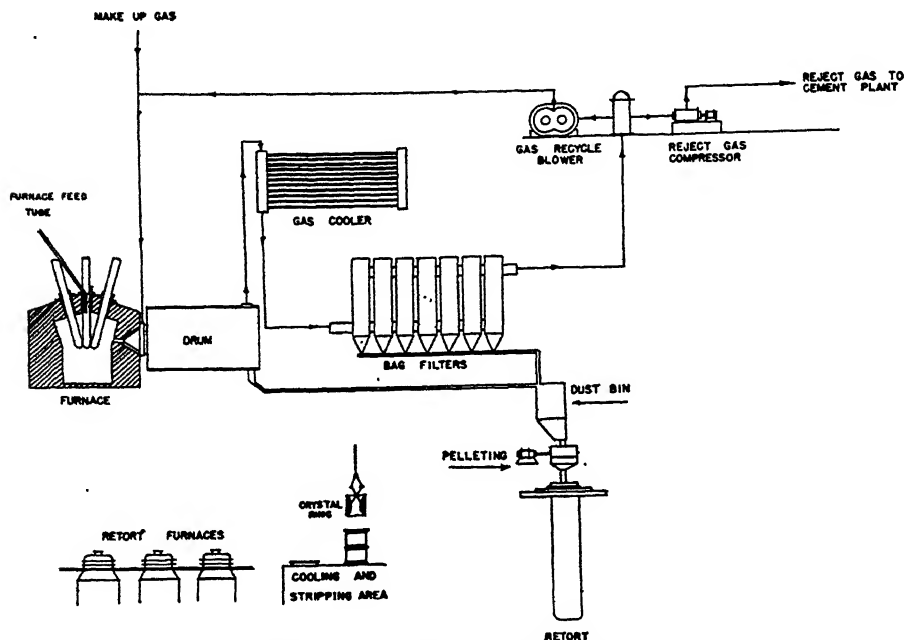


FIG. 1.—SCHEMATIC FLOWSHEET, CARBOTHERMIC PROCESS.

A description of the process at Permanente is best approached by following the flow of materials. However, to better understand the flow a summary of basic principles is given:

The function of the plant is to produce metallic magnesium and magnesium alloys. This is accomplished by reducing magnesia with carbon in electric furnaces. The reduction products, CO and magnesium vapor, issue continuously from the furnaces and are shock-chilled immediately by a continuous stream of natural gas. This produces a fine magnesium dust contaminated by the back reaction with fine carbon and magnesia. The magnesium is extracted from this dust by vacuum sublimation, which produces consolidated crystals of magnesium of exceptional purity. The

The dolomite—which, by the way, is a true dolomite, the calcium and magnesium carbonates being in molecular proportions—is quarried in the hills east of Salinas, California, and calcined to the double oxide. The calcine is trucked to the Permanente sea-water magnesia plant north of Salinas, on the edge of Monterey Bay. There the lime content of the calcined dolomite is replaced by the magnesium ions from the sea water and the magnesium is precipitated as the hydroxide. This is washed, filtered and dehydrated, producing a magnesium oxide of 96 per cent purity. A typical analysis is shown in Table 2.

The magnesium oxide is then transported by truck to Permanente and loaded into a compartmentalized storage bin having a capacity of 350 tons MgO and 200 tons of

coke. Petroleum coke low in ash and sulphur and reasonably high in volatiles is purchased from various refiners. A typical analysis of the coke is: volatile matter, 16.0 per cent; H_2O , 0.5;* fixed carbon, 81.1; ash, 2.4. The magnesia and carbon are fed from the bin through automatic proportioning devices in the ratio of 76 per cent magnesia to 24 per cent coke. The two materials are ground together to 90 per cent minus 200-mesh, in a Traylor two-

TABLE 2.—*Typical Analysis of Magnesia, Moss Landing Plant*

	PER CENT		PER CENT
Ignition loss.....	0.26	MgO.....	96.42
SiO ₂	1.19	NaCl.....	0.02
R ₂ O ₃	0.37	SO ₂	0.32
CaO.....	1.42		100.00

compartment ball mill, 7-ft. diameter by 26 ft. long.

The mixed coke and magnesia is conveyed by screw conveyors to a battery of three Komarek-Greaves pelleting presses, where oval pellets slightly larger than walnuts are formed. The sole reason for using high-volatile coke is to make a pelletable mixture.

The pellets are transported by belt conveyor from a level above to the main reduction plant, where they are distributed to the air-locked feed bins of each of the furnaces. Fines are screened from these pellets just before the bins are loaded. The bins are above each reduction furnace and are so valved with full round 8-in. plug cocks hydraulically actuated that furnace pressure cannot escape up through the feed system. Air is purged from the upper bin by a stream of nitrogen. The second bin is under an atmosphere of hydrogen. The pellets drop from the second bin to a rotary disk feeder driven by a varidrive motor. Pellets are fed from the disk feeder at a constant rate down a 6-in. stainless-steel pipe, which drops the feed vertically into the center of the three-phase sub-

merged arc furnace. The temperature of the furnace is maintained at 1950° to 2050°C., as measured by an optical pyrometer, which "sees" the furnace bed through a peep tube next to the feed tube. At this temperature the reaction time for such a pellet is probably in the magnitude of several seconds—perhaps even a minute.

Each reduction furnace consists of a carbon crucible, cylindrical in shape, with internally tapered walls, the internal diameter at the level of the coke bed being approximately 60 in. The crucible wall at its thinnest point at the junction of the roof is 4 in. thick. The roof is constructed of keyed carbon blocks 18 in. thick. The electrodes are 20-in. diameter, machined surfaced graphite. They enter through three holes in the roof 120° apart and each electrode is on an angle with the vertical of 11°. The crucible is surrounded by an average thickness of about 4 ft. of fine gas carbon for insulation, and the whole assembly is within a pressure-tight steel shell 16 ft. in diameter, 16 ft. high, with a flat bottom and an obtuse conical roof of nonmagnetic steel. The design and development of the present glands or stuffing boxes through which the electrodes are introduced into the furnace was a major triumph after the repeated failures of the glands originally designed, supposedly after the glands used at the Korean plant.

The furnace is operated at voltages from 150 to 170 and at current rates up to 35,000 amp. per phase. The bus bar from transformer to each of the three 20-in. diameter graphite electrodes is balanced for equal reactance in each leg. The electrode travel is controlled by reversible d.c. motors in an amplidyne circuit, so that each electrode "hunts" for equal current, thus maintaining balance in each phase.

The magnesia-carbon pellets react continuously and the reaction gases, CO and magnesium escape from the crucible through a 10-in. diameter hole in the vertical wall of the crucible, about 8 in. above

* The water is almost completely driven off during grinding.

the coke bed, where immediately they enter the shock-chilling cone. The oil-cooled tip of the cone is recessed from the furnace shell right up to the outlet hole in the crucible and surrounds the hole.

gas to furnace feed is maintained so as not to exceed a temperature of 250°C. in the drum. The function of the gas cooler is to lower this temperature to 80°C., to protect the woolen bag filters. Each bag-filter unit

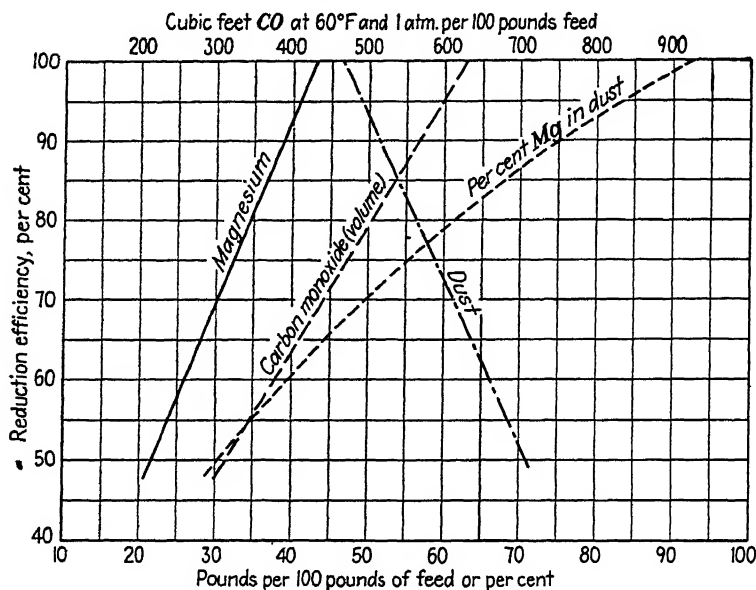


FIG. 2.—PRODUCTS OF REDUCTION FURNACES.

Pellet feed consisting of:

	PER CENT
Sea-water MgO:	
Ignition loss.....	0.26
SiO ₂	1.19
R ₂ O ₃	0.37
CaO.....	1.42
MgO.....	96.42
NaCl.....	0.02
SO ₂	0.32

	PER CENT
Petroleum coke:	
Volatile matter.....	16.5
Water.....	0.5
Fixed carbon.....	81.1
Ash.....	2.4
Sulphur 1.3 per cent	

The shock-chilled magnesium dust and natural gas are conducted under their own pressure from the crucible, through the chilling cone to a drum that is 15 ft. in diameter and 34 ft. horizontally. The function of this drum has been the subject of some discussion. While very little of the shock-chilled magnesium dust settles in this drum (20 per cent at the outside) it does provide a gas cushion. The major portion of the magnesium dust, however, is gas-borne from the drum through a 24-in. line to a surface heat exchanger that is externally water cooled, and thence to the bag filters. The ratio of shock-chilling

is an arrangement of 14 cylinders, 7 on each side of a gas header, and each cylinder contains 28 bags 7 in. in diameter and 10 ft. long. The dust is removed from the bag filters by an automatic pneumatically operated device, which closes the dampers on each cylinder and shakes the bags in proper sequence. The magnesium dust is conveyed from beneath the bag filters to dust bins above the extrusion presses. This magnesium dust contains approximately 50 per cent magnesium metal, 20 per cent carbon and 30 per cent MgO.

The excess carbon (above stoichiometric quantities formed by the back reaction

$\text{CO} + \text{Mg} \rightarrow \text{MgO} + \text{C}$) comes from four sources: (1) the electrodes, which are consumed at the rate of about 18 in. for 24 hr.; (2) some consumption of the metallurgical coke bed in which the arc is submerged (this is made up in small increments with the furnace feed); (3) the volatile content in the petroleum coke, which is largely carbon by weight; (4) a small amount of cracking of the higher hydrocarbon constituents in the natural gas. A ratio of 50 per cent magnesium to 20 per cent magnesium oxide represents an over-all conversion efficiency of magnesium oxide to magnesium metal of slightly over 80 per cent. Fig. 2 shows the quantity relations at various chilling efficiencies. The curves for "dust" and "per cent Mg in dust" assume the absence of all other carbon except that present by virtue of back reaction.

SUBLIMATION

The magnesium dust has a particle size below the resolving power of optical microscopes, and investigations indicate the size to be in the order of 0.1 to 0.6 microns. It is necessary to distill or sublime the magnesium from this dust in order to obtain pure compact metal that can be handled in the air. The dust itself is not amenable to sublimation at reduced pressures unless it is consolidated into briquets or tablets. Permanente experienced extreme difficulty in tableting this dust with presses designed in accordance with oral description of the presses used at Konan. In order to produce metal immediately for the war effort while waiting for the development of a suitable press, a simple but somewhat messy method was immediately installed. The principle was to thoroughly mix the dust with an asphalt cutback in cleaning solvent or kerosene and to extrude this pasty mixture into the sublimation retorts, where the solvent was first distilled and the asphalt coked to form a nondusting structure amenable to sublimation. All the metal produced at Permanente to date has been produced by

this method except a few tons now being sublimed from dry tablets made on a small pilot press.

The sublimation retorts, known as "bottles," are vertical, cylindrical vessels 56 in. in diameter by 22 ft. high, made of firebox iron. The crystal condenser consists of a cylindrical steel liner that extends from the top of the retort down 8 ft. The retort charge, whether it is the cutback asphalt mixture locally known as "goop" or the newer dry tablets, is loaded around a central core, 33 in. in diameter. This maintains the charge against the walls of the retort and the core is so perforated as to provide ready escape for the metal vapors. Between the sublimation and condensing portion of the retort is a heat dam, which has taken many and various forms, and which influences the location and type of crystals produced.

The entire bottle is lowered into a retort furnace, which is a vertical steel shell lined with insulating and firebrick; the inside is festooned with Nichrome resistance heaters to a capacity of 120 kw. When the bottle is lowered into the furnace, flanges just under the lid match with flanges on the furnace, forming a gastight enclosure. This is required because the space outside the bottle must be maintained under a vacuum to prevent collapse of the bottle operating under vacuum. The lid of the bottle is a bumped head with external water jacket and provided with vacuum connections.

The retort furnace is connected to a central vacuum system consisting of seven two-stage Fuller rotary vacuum pumps, which maintain an absolute pressure of approximately 3 mm. Hg. In production with the "goop" the vacuum connection from the lid of the bottle is connected to a central solvent-condensing system operating under modest vacuum. When the solvent distillation and coking of the asphalt is complete, the vacuum valves are closed and the line reconnected to individual Kinney single-stage vacuum pumps

operating at 100 cu. ft. per min., which bring the pressure down to 0.2 mm. Hg. The solvent distillation and coking generally require from 24 to 36 hr., depending on

stations, and after stripping return them to the loading stations. At the cooling stations the bottles are lowered into wells and reconnected to a low-pressure supply

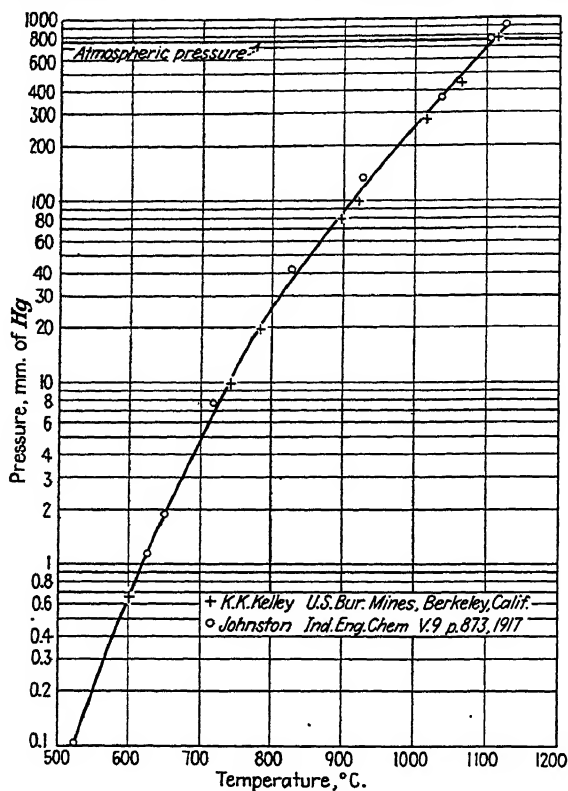


FIG. 3.—VAPOR PRESSURE OF MAGNESIUM.

the consistency of the "goop." By this time the retort has been brought up to sublimation temperature, 800°C., and sublimation proceeds for another 48 hr., which yields an average crystal ring of 2200 lb. Fig. 3 is the vapor-pressure curve for magnesium.

Before the retort is stripped, the vacuum is broken by admission of hydrogen and the furnace vacuum is simultaneously broken by admission of air. It is then transported by one of two large gantry cranes that handle all the bottles from the loading stations to the 128 retort furnaces, and from the retort furnaces to the cooling

of hydrogen during the cooling, which requires 12 to 15 hours.

When a bottle is sufficiently cool to permit removal of the crystals, hydrogen is evacuated and replaced by nitrogen. The bottle is then moved by crane to the stripping area, where the lid is removed and the condenser liner, with the crystal ring adhering to it, is removed. The condenser liner is of segmented construction, to facilitate harvesting of the crystals. The crystals are weighed and sent to the adjacent foundry on push trucks equipped with suitable bins. The crystals are then melted down and alloyed to produce the principal alloys now required in the war effort.

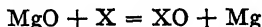
Thermal Production of Magnesium—Pilot-plant Studies on the Retort Ferrosilicon Process

BY L. M. PIDGEON* AND W. A. ALEXANDER†

(New York Meeting, February 1944)

METALLIC magnesium and similar metals near the top of the electromotive series have been commercially produced by the electrolysis of a suitable molten salt. Despite the success of electrolysis, sufficient inherent objections exist to justify the search for a direct reduction method. Such a method would widen the choice of raw materials, relax the rigid electrolytic requirements of raw-material purity, and, by obviating direct current, offer simplicity of plant equipment. This paper describes the pilot-plant development of one such method, which has subsequently formed the basis of operation of six commercial plants—one in Canada and five in the United States.^{1,2}

Unlike aluminum, magnesium is volatile at relatively low temperatures. This physical property, which produces its greater inflammability, also offers possibilities of direct reduction that are not available with aluminum. In the basic reaction



if X is nonvolatile, the reaction may be forced to the right at high temperatures by the evolution of magnesium vapor, despite the large negative value of the heat of reaction which is almost bound to follow the use of any available commercial reducing agent.

The cheapest X, of course, is carbon, but

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¹ References are on page 352.

this notable advantage is modified by the production of a volatile oxide CO, so that both Mg and CO are evolved simultaneously. Elaborate devices are required to shock-cool the equilibrium mixture in order to prevent back reaction. At best, a pyrophoric powder is produced, requiring redistillation to provide marketable metal. The practical development of this process is due to F. Hansgirg,³ and his methods have recently been given a trial on a grand scale in the plant at Permanente, California, and smaller plants were previously built in Austria, England and Japan.

A second class of reducing agents is available, those which produce nonvolatile oxides. When XO and X are relatively nonvolatile, magnesium is the only volatile member of the system. It may be evolved in a simple distillation step and condensed without the formation of powder.

Two basic requirements must be fulfilled in order that such a reaction may proceed:

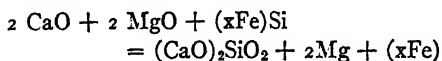
1. The reducing agent when heated to a reasonable temperature in presence of MgO must cause the production of an appreciable equilibrium vapor pressure of magnesium. This magnesium must be removed continuously.

2. A supply of heat must be maintained.

In order to fulfill the first requirement, operations must be conducted in vacuo or in a stream of H₂. Owing to its greater efficacy and relative safety, vacuum has been employed in the work to be described.

The choice of a suitable reducing agent formed the subject of an extensive series

of small-scale experiments, which examined the reactions between calcined dolomite, magnesia and calcined serpentine and such reducing agents as silicon, aluminum, calcium carbide and calcium silicide. In a separate publication, one of the authors will describe this work and discuss the mechanism of reactions of this type in detail. It was concluded that the greatest commercial possibilities were offered by the reaction between calcined dolomite and silicon in the form of ferrosilicon:



The availability of dolomite is an outstanding advantage. The lime forms a silicate in the residue, thereby preventing loss of available magnesia by a similar reaction. Ferrosilicon was the cheapest reducing agent (in dollars per equivalent) of this type available at the time this work was initiated. Aluminum and aluminum-silicon alloys are chemically more attractive, but the former is too expensive in normal times while the latter has been unavailable in commercial quantities and has yet to be produced as cheaply as ferrosilicon on an equivalent basis.

The reaction given above has been known for many years, being described by Bleeker and Morrison⁴ and by Grosvenor,⁵ neither of whom produced successful devices for carrying it out commercially.

The reactants are solids and the residue remaining after magnesium vapor is evolved is a solid. Under such conditions, the ferrosilicon and calcined dolomite must be reasonably finely ground to permit the reaction to proceed to completion. In this powdered form, a large-scale reaction system is impossible, since neither could heat penetrate into the mass nor magnesium vapor be evolved. Obviously, the charge must be pressed into the form of briquettes or pellets to achieve a workable physical condition.

Some 600 small-scale experiments carried

out in apparatus of various designs proved that small briquettes would react at reasonable velocities at a temperature of 1100°C. With this fact established, the next step was to develop an apparatus for conducting the reaction on a commercial scale.

The difficulties to be encountered will be evident from a consideration of the fundamental requirements of the reaction. A suitable apparatus must be capable of:

1. Heating calcined dolomite and ferrosilicon in briquetted form to a reacting temperature and maintaining a supply of heat at this temperature sufficient to overcome the endothermic reaction.
2. Receiving a solid charge of briquettes and discharging a residue of similar shape and form. The reaction zone must be in vacuo during evolution of magnesium vapor.
3. Removing magnesium vapor continuously and completely under nonoxidizing conditions.
4. Condensing the magnesium vapor in a form capable of safe handling and ready conversion to ingots or other marketable form. The purity of the latter must be as high as that of ingots already available by established commercial production methods or, preferably, higher.

The development of an apparatus fulfilling these requirements presents formidable problems. It was considered that a continuous apparatus was beyond the available technique and pilot-plant research facilities. Thus, despite the undisputed advantages of such a process, it has not been considered in the work to be described.

The stipulation that the reaction system must be loaded, unloaded and evacuated suggested a retort or autoclave, with the minimum number of openings, heated at the closed end, with the open end protruding from the hot zone, water-cooled and fitted with a vacuum-tight closure. Such an apparatus may be loaded and unloaded as a batch operation, and may

readily be evacuated. Since the magnesium vapor is condensed in the cool part of the apparatus soon after formation, all handling of this very reactive gas is obviated.

Since small-scale experiments had established that the reaction would proceed at reasonable rates at a temperature of 1100°C ., the feasibility of a retort of heat-resisting steel was indicated. The wall of such a retort withstands the pressure of the atmosphere, contains the magnesium vapor, and forms a hot wall through which the heat necessary to drive the reaction must pass to the charge. This, of course, is a serious objection, since it limits the temperature gradient and size of retort that may be employed. On the other hand, the fundamental simplicity of the apparatus appears to outweigh its disadvantages in the present state of development at least. For convenience of loading and furnace design, a horizontal disposition of retorts was chosen.

Preliminary Experiments in Steel Retorts

Early experiments were carried out in 2-in. Ni-Cr steel tubes, and the results of previous work were duplicated. Yields of the order of 75 to 80 per cent were obtained in these small tubes. Experiments on a larger scale were indicated and 6-in. and 8-in. short retorts were obtained, capable of holding respectively some 5 lb. and 18 lb. of briquettes and producing from $\frac{1}{2}$ to 3 lb. Mg per experiment.

From the results of small-scale experiments, it was known that magnesium must be condensed at fairly high temperatures in order to obtain a coherent deposit under commercial vacuum conditions, where the lowest pressures readily attainable are approx. 0.1 mm. Hg. (The temperature of the Mg deposit should be of the order of 400° to 450°C . See Fig. 1.)

It was assumed that the addition of air to this hot Mg deposit would inevitably result in ignition.⁶ Early experiments,

therefore, were conducted by allowing the retorts to cool before vacuum was broken. Satisfactory yields and deposits were obtained, but it was soon established that heat-resisting steels would not stand such treatment for long and remain vacuum-tight. The process would succeed only if the retort remained substantially at the operating temperature throughout the charging and reduction operations. Thus, vacuum must be broken, and the retort opened with the magnesium deposit *in situ*. The danger of fire is very real and the patent literature describes various mechanical devices for isolating the magnesium deposit during this operation (e.g., ref. 6).

It seemed that practical operation would follow only if the vacuum could be broken with air without the use of complicated devices. It was found that this result could be achieved if the magnesium was collected in a dense deposit that was free of alkali metals. A 3-ft. retort 4 in. i.d., which was a sand casting with $\frac{1}{2}$ -in. walls of 35 Ni, 15 Cr steel, was placed in a tilting gas furnace so that the contents could be dumped at the termination of a "run." The retort, shown in Fig. 1, was held substantially at a constant temperature throughout the whole operation. One pound of magnesium was regularly made in this apparatus, using briquettes $\frac{3}{4}$ by $\frac{1}{4}$ in. made in a single-punch automatic pill press. Silicon efficiencies of 80 per cent were obtained in 3 hr. at a firing temperature of 1130°C . A fresh charge was added to the hot retort, the top was left off until water evolution ceased, the system was evacuated for 3 hr., then the vacuum was broken, the magnesium and charge removed and the cycle repeated.

Results of these experiments were considered sufficiently promising to justify the construction of a larger pilot plant. This type of work is not carried out by the National Research Council, and the authors were fortunate in obtaining the support of Dominion Magnesium Limited,

which financed the work to be described. It was decided to proceed with the construction of a pilot plant utilizing retorts of commercial size. If operations were suc-

cessful with one or two such retorts, a commercial plant could be built simply by increasing the number of retort units.

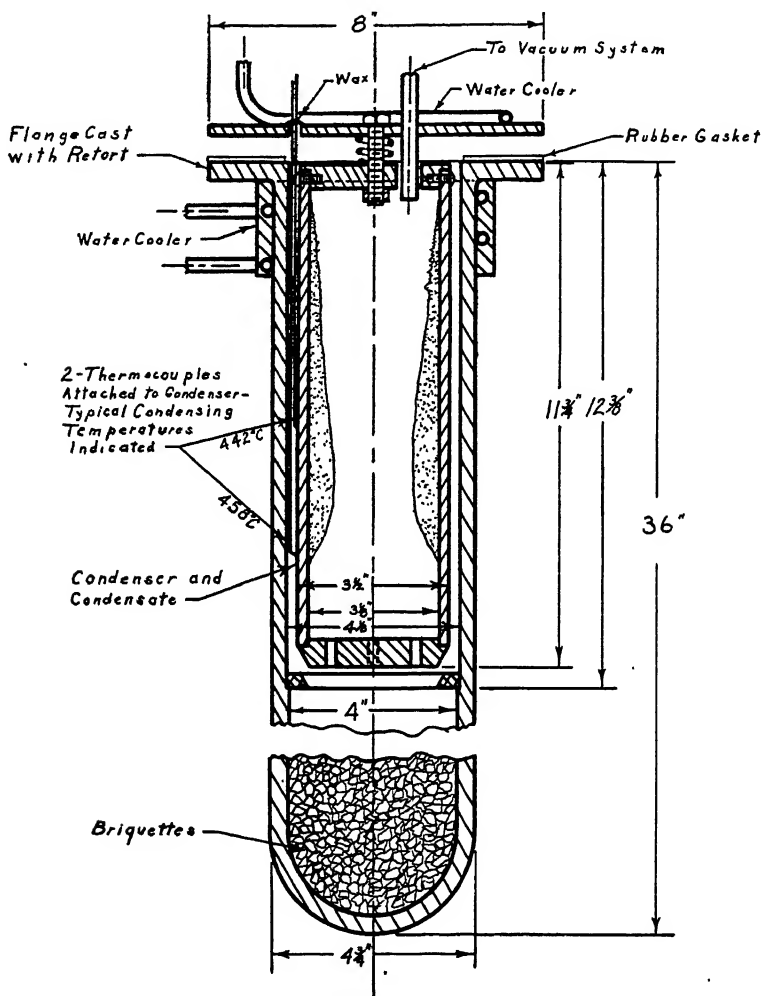


FIG. 1.—FOUR-INCH RETORT.

cessful with one or two such retorts, a commercial plant could be built simply by increasing the number of retort units.

THE PILOT PLANT

Retorts

Since the retorts are the heart of the process, they will be described first. The

retorts employed in the preliminary pilot plant are shown in Figs. 2, 3 and 4. The first retorts were 8 in. in diameter, this size being chosen partly from a considera-

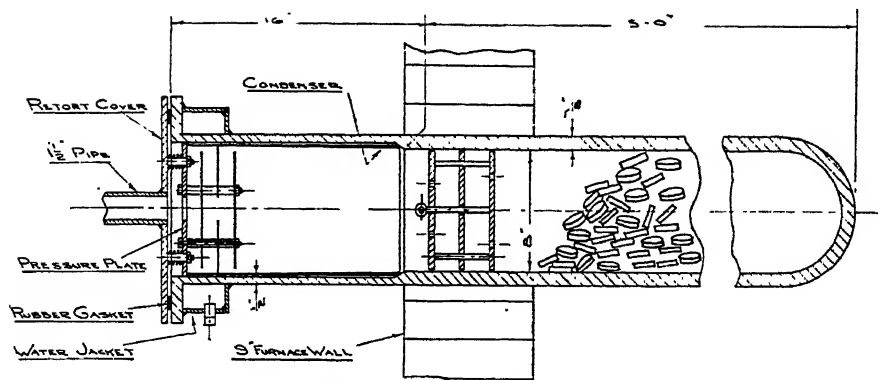


FIG. 2.—EIGHT-INCH RETORT.

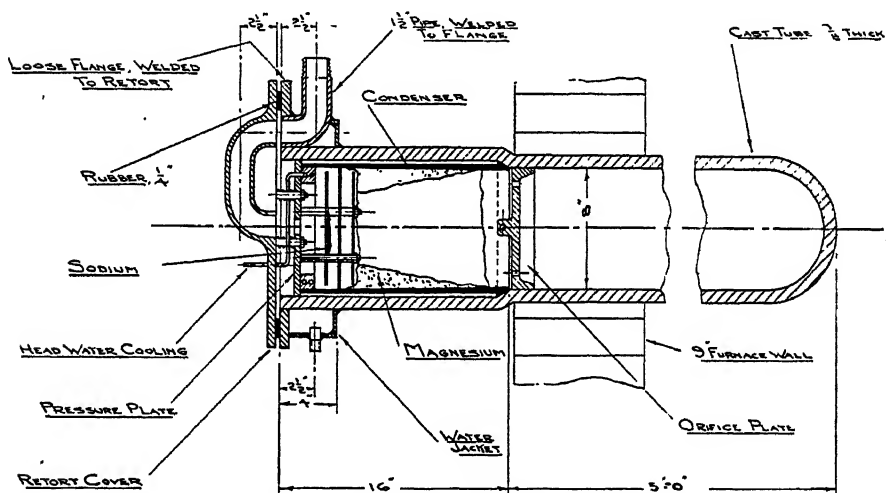


FIG. 3.—EIGHT-INCH DIAMETER RETORT.

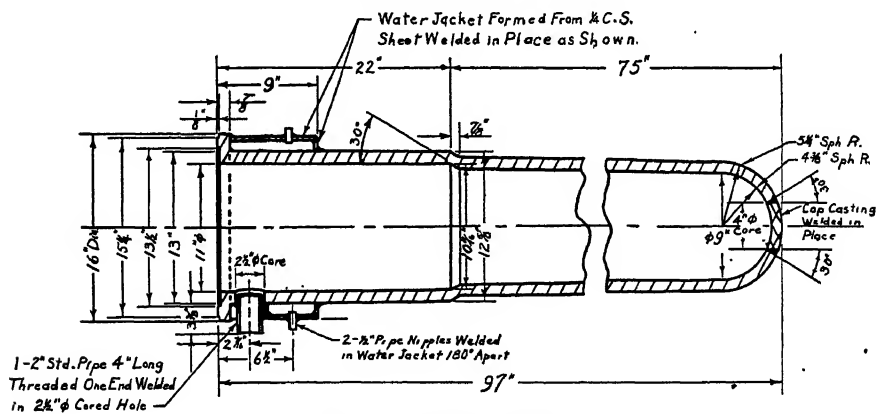


FIG. 4.—TEN-INCH RETORT.

called for a wall in excess of $1\frac{1}{2}$ in. This was considered an excessive amount of metal and suggested the choice of an 8-in. retort. Eight-inch retorts with a wall

Condenser Design

The condensers are shown in Figs. 2, 3 and 5. Previous experience indicated that the magnesium must be deposited at a

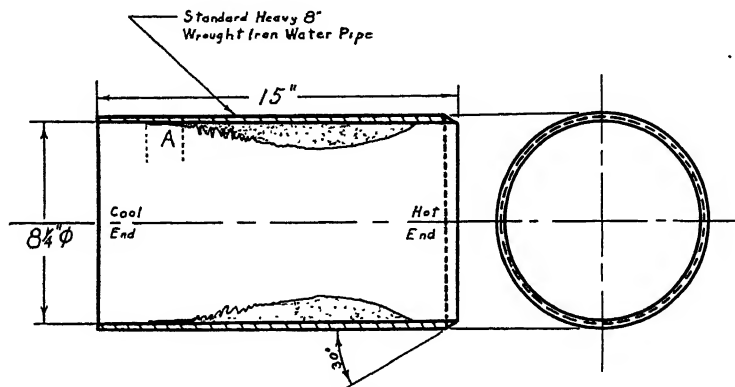


FIG. 5.—CROSS SECTION OF CONDENSER AND CONDENSATE WITHOUT BAFFLES.

thickness of $\frac{3}{8}$ in. were chosen, and such retorts have given nine months' life without collapse in full-scale plant operation, while 90 per cent of the retorts were still in operation at 359 days.

After several months of successful pilot-plant operations with 8-in. retorts, a 10-in. retort was designed (Fig. 4), incorporating improvements eventually used in the plant. The flexible vacuum connections were eliminated by lengthening the condenser section. Vacuum connections in early retorts were made through the removable closure, so that the retort could be rotated if necessary. The wall thickness was increased to 1 in. as a result of experience with the 8-in. retorts.

All the retorts were sand cast, and most of them were of the nominal composition of 35 Ni, 15 Cr. One retort of composition 28 Cr, 12 Ni was tried. After one month of operation, this retort developed a crack, owing to an unusual accident. Since the furnace held but two retorts, and the retort life was 6 to 9 months, no conclusions regarding ideal composition could be expected nor were forthcoming before the design of the full-scale plant was initiated.

fairly high temperature to avoid any semblance of "vapor-phase" condensation. As shown in Fig. 1, thermocouples peened into the outside of the condenser read temperatures of 450°C . during deposition of an ideal dense deposit. While the deposit will find its own "level" in the falling temperature gradient existing in the cooling region of the retort, some of the metal will escape the "ideal" region and condense at too low a temperature. A typical deposit formed under these conditions is shown in Fig. 5.

In the region A, deposition has taken place at an undesirably low temperature and loose crystals are formed, which are readily inflammable and cause high melting loss.

A further difficulty was encountered when large amounts of charge were employed. Small amounts of alkali metals are present in most dolomites. These were reduced, and, being more volatile than magnesium, were concentrated in the region A, just where the magnesium was loosely deposited and in a readily ignitable condition. When air was admitted to the retort, the hot alkali metals ignited and

the fire was generally transmitted to the Mg "crown," resulting in partial or total loss.

assembly, which prevented any close approach to complete thermal isolation. The heavy pins shown in the diagram

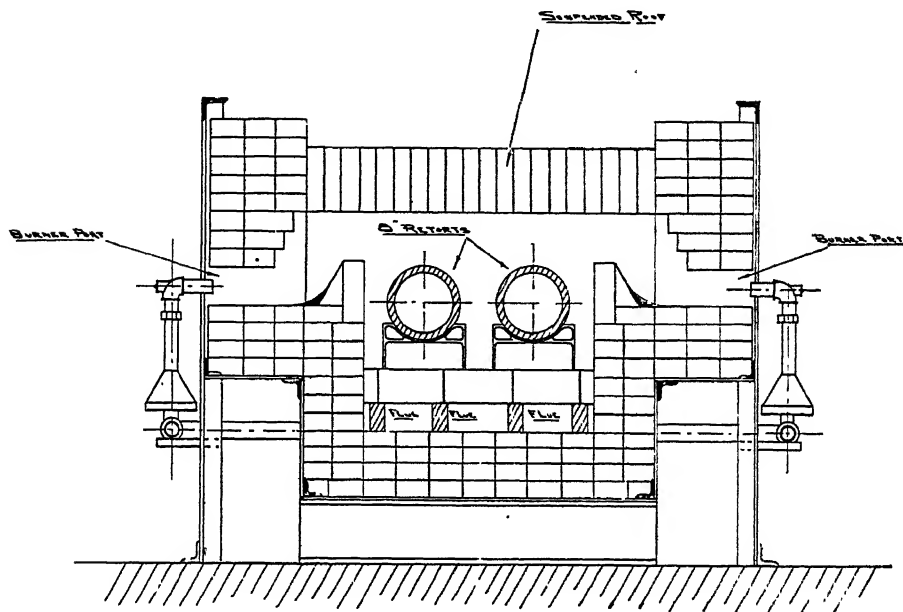


FIG. 6.—RETORT FURNACE, TYPICAL CROSS SECTION THROUGH BURNER PORTS.

Under ideal conditions the magnesium must be deflected against the condenser before reaching *A*, and at the same time a condensing space for alkali metals must be provided separate from the magnesium. These conditions were fulfilled by the arrangement shown in Fig. 3.

The position and number of baffle plates was varied, retaining at all times the first plate with the opening near the condenser. At all times, the assembly should be set well towards the "hot" end to "crowd" the deposit to the shape indicated in Figs. 3 and 12.

The first plate (hot end) should theoretically be thermally isolated from the rest of the system, in which case no Mg will condense thereon, since the plate cannot lose the latent heat of condensation. The attainment of this ideal was found to be limited in practice by considerations of mechanical strength and ruggedness of the

carried more heat from the front plate than was desirable.

The springs on the condenser covers were included to hold the condenser against the tapered seating. Omission of these springs permitted sufficient leakage of magnesium vapor to the space between the retort wall and condenser to increase greatly the difficulty of removal of the latter. This was particularly true with the early 8-in. retorts, where the depth of the seating was small as measured perpendicular to the axis of the retort. The difficulty largely disappeared in the 10-in. retort, where the longer condenser permitted a smaller inclination of the condenser to the horizontal axis of the retort, with a consequently smaller opening and less leakage. It was found eventually that the springs could be omitted, provided the retort condenser section was cleaned after each run.

The first design called for a removable head without water cooling, but the initial trial of this arrangement was made before the baffles were developed, with the result that the head was exposed to the radiation from the heated section of the retort and became so hot as to burn the rubber vacuum gasket. The internal water cooler shown in Fig. 3 was then added to prevent the overheating of the head. The baffle systems shown in Figs. 2 and 3 were then developed. With the insulation from radiation provided by these baffles, it was soon found that the internal coolers were unnecessary and they were discarded. Fig. 2 shows the later scheme of baffles, retort cover, vacuum connection and radiation shield.

A radiation shield between the reacting charge and the condenser is shown in Figs. 2 and 3. The design shown in Fig. 3 was cast in 35-15 nichrome steel and originally was intended to hold a layer of insulating brick. When this design proved too fragile for pilot-plant operation, the baffle type shown in Fig. 2 was designed and found to be satisfactory. Mild steel oxidized fairly rapidly at the temperature of operation, which was in the neighborhood of 800°C. Stainless steel had a long life under these conditions, and the question of material used becomes one of economy.

The radiation shield affects the position of the deposit to some extent. Without a shield, this deposit will be crowded to the back of the condenser. The shield also assists in maintaining the temperature of the front of the charge and, at the same time, decreasing furnace heat losses. With a short retort, these factors are very important; while the larger the retort, the less important do cold-end losses become. Thus, if the benefits are not considered of sufficient importance to compensate for the complication, the retort will operate without any shield, as was demonstrated on many occasions in the pilot plant. A minor but practical advantage of the shield

is that it prevents briquettes from getting into the condensed metal, a definite possibility in plant operations with unskilled labor.

It was important to obtain the condensate in the correct position to obtain high "density" and complete separation of alkali metals. The position of the condensate is controlled by

1. Position of retort in furnace and thickness of furnace wall.
2. Radiation shield position and construction.
3. Position of the condenser plates.
4. Position of water cooler.

The order of importance is as indicated. With 1 and 4 fixed for a given system, 2 and 3 may be varied to produce the optimum deposit. As will be seen later, the pressure of inert gas in the system exerts a powerful effect on the nature and position of the deposit.

Furnace Design

The design and construction of the furnace is shown in Fig. 6. The furnace was direct gas fired. The flame did not impinge on the retorts, but the latter were exposed to the products of combustion together with excess air. The burner ports and baffle were constructed of dense firebrick while the remainder were insulating brick.

Temperature control was achieved by a thermocouple-controlled motor valve in a by-pass gas line to the burners. A small amount of auxiliary gas was automatically turned on and off by the controller. The thermocouple was suspended between the retorts in the center of the furnace. The controlling indicator was set to achieve the desired retort temperature. The latter was measured by optical pyrometer. The burners had individual valves, and were adjusted by hand to secure a uniform temperature throughout the furnace. Once this was achieved, the single thermocouple controlled the gas supply. The retorts

rested upon special saddles, being supported at two points in the heated section. The supports were altered to take the 10-in. retort, only one of which could be accommodated by the furnace.

The furnace was fired by Ottawa City gas of the following nominal composition: CO₂, 2.75 per cent; O₂, 0.56; illuminants, 7.56; CO, 33.6; H₂, 35.0; CH₄, 12.6; C₂H₆, 0.43; N₂, 7.5; free H₂S, none; CS₂, very little; organic sulphur, very small.

The calorific value of the gas was about 490 B.t.u. per cubic foot and was supplied at a pressure of about 11 in. of water. In the interests of retort life, the furnace was operated in such a manner as to maintain an oxidizing atmosphere at all times, as the following analysis indicates:

Auxiliary Gas	Analysis, Per Cent		
	CO ₂	O ₂	CO
On.....	7.9	5.3	0.0
Off.....	8.4	4.4	0.0

These analyses were done on single samples.

Preheating

The reaction mixture for this process is largely composed of free lime and magnesia and therefore is an excellent absorbent for water and carbon dioxide. Thus, in spite of normal precautions, including thorough calcination, there will be a volatile constituent in all charges that must be removed before the reaction proceeds, since the magnesium vapor will be oxidized by these substances.

Since the basis of the process comprises the charging of the reduction apparatus at the reaction temperature, the gases that react with magnesium vapor must be removed as rapidly as possible, to avoid loss of yield and to maintain the quality of the deposit, which is impaired by high pressures. A degassing operation must be carried out in the retort, or partly before

the charge is added to the retort. This degassing operation is discussed under the term "preheating."

Theoretically, a relatively gas-free charge should result from heating to a sufficiently high temperature to drive off all volatile matter. Practically, however, some silicon oxidizes if this heating takes place in an oxidizing atmosphere. The mechanism of the oxidation is not entirely clear. It could conceivably be the direct union of silicon with free oxygen or oxygen from oxides such as water and carbon dioxide, or perhaps the oxidation of silicon by magnesia with liberation of magnesium vapors, which are immediately oxidized by oxygen from the same sources. Thermodynamic calculations have shown that the equilibrium pressure of magnesium vapor is appreciable at 1100°C. in this system, and a patent by Seliger⁷ would indicate that silicides might be formed in this temperature range. Whatever the details of the oxidation, the net result is essentially the conversion of silicon to silica with the formation of hydrogen, carbon monoxide, carbon, etc. Briquettes heated at 1150° in air show progressive oxidation of silicon.

In this work, three methods of preheating or degassing were examined:

1. A short, intense preheating at the operating or reduction temperature of the furnace.
2. A longer time of preheating at a lower temperature at which the oxidation of silicon is practically eliminated.
3. Closing the retort immediately after charging at the operating temperature.

The recoveries of magnesium were appreciably affected by the preheating method employed. Method 3 invariably gave the best recoveries, but placed a heavier burden on the pumping system.

Method 2 gave nearly as good results and was generally employed in the pilot plant. The preheating was carried out in electrically heated, sloping 8-in. iron tubes, since this was the most convenient device

available. The strong briquettes produced in the large piston press suffered little breakage during this operation.

Method 1 gave definitely lower yields in these short retorts. The reduction in yield increased as the time of preheating or "burn-off" was increased. In this connection, it should be mentioned that the magnitude of the loss during preheating at the operating temperature will depend on the geometry of the system. Undoubtedly, a large part of the reduction in yield is due to the oxidation of the silicon by air that circulates through the charge. The access of air is less, of course, in a longer retort and a larger mass of briquettes produces a more effective inert atmosphere by the reduction of water. Thus, early experience with a short 8-in. retort showed a maximum reduction in yield compared with longer retorts.

A further difference between pilot-plant and full-scale plant operation occurs in the handling and quality of the briquettes. The briquettes used in the pilot plant were considerably harder, and hence more resistant to breakage during preheating, than those produced in full-scale plant operation. As is pointed out below, fragments, and particularly dust, in the charge cause a definite lowering of silicon efficiencies.

Vacuum System

The presence of inert gas existing in the vacuum system plays a vital role in the evolution of magnesium vapor and the collection of solid metal. From theoretical considerations, it would be expected that the lower the pressure the faster the reaction would proceed, since the magnesium vapor in equilibrium with the charge would be removed more readily.

The effect of pressure was examined in small-scale experiments, giving results shown in Table 1.

In this small system, and with the small

briquettes, the difference between the yield at 0.5-mm. pressure and at 0.0005-mm. pressure was 0.8 per cent, an amount less than the experimental error.

With pressure exerting so little effect in this range with the 2-in. retort, it is not surprising that in the 8-in. and 10-in. retorts no improvement in yield has been

TABLE 1.—*Reaction in 2-inch Retort*
Temperature, 1100°C. Time, 30 minutes.
75 per cent FeSi. Portage du Fort dolomite.
Briquettes $\frac{3}{8}$ -inch (irregular fragments).
Charge 100 Grams.

Pressure (H ₂), mm. Hg.....	0.0005	5	10
Reaction, per cent.	77	64	45

noted at pressures lower than 0.5 mm. Isolated experiments at even higher pressures gave good yield. In October 1941, an oil-vapor diffusion pump was installed in the pilot plant. At pressures of 0.002 mm. Hg, no improvement in yield was achieved compared with ordinary operating pressure of the order of 0.1 to 0.2 millimeter.

Quite another reason exists for desiring low pressures. If an appreciable pressure of inert gas exists in the system, the magnesium vapor must pass through a blanket of relatively cold inert gas to reach the condenser. Vapor-phase condensation is encouraged, tending to produce powder or at least a loose deposit. While this undesirable situation may be controlled to some extent by raising the condenser temperature, the best deposits invariably are obtained by lowering the residual gas pressure.

During the course of the reduction cycle, three stages of evacuation exist: (1) removal of air from the retort, (2) removal of volatile constituents of charge (pull-down period), (3) maintenance of vacuum during magnesium evolution (holding period). Fig. 7 shows typical pressures during evacuation of 8-in. and 10-in. retorts. No definite boundaries are included for the three periods. Nevertheless,

each "period" makes different demands on the vacuum system.

During the initial evacuation, the pressure rapidly falls from atmospheric to the

considerable gas at pressures of the order of 0.2 to 5 mm. Hg.

During the final or holding period, theoretically, zero pumping rate is de-

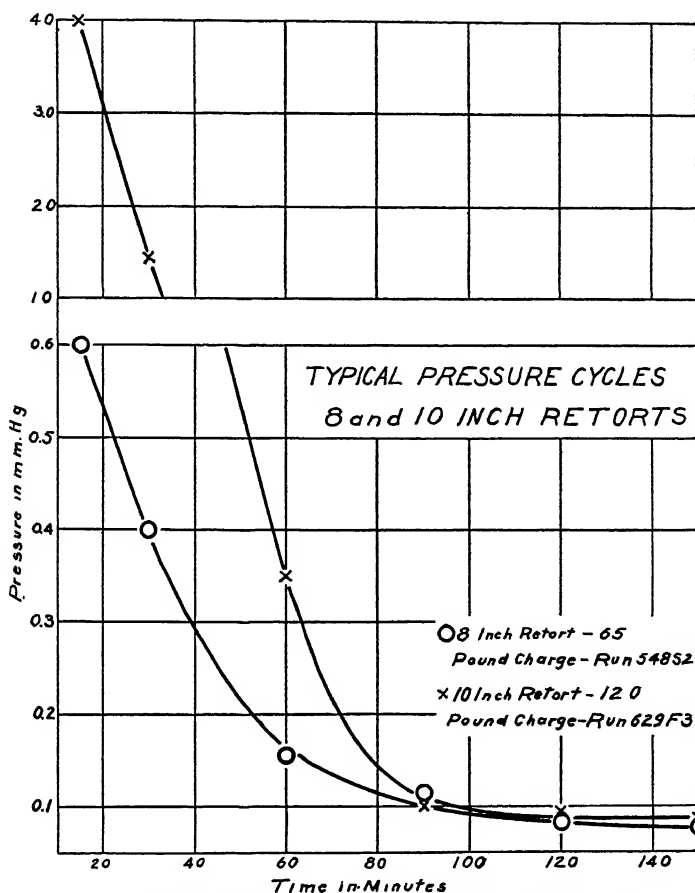


FIG. 7.—TYPICAL PRESSURE CYCLES OF 8 AND 10-INCH RETORTS.

order of 1 to 5 mm., owing to the high volumetric efficiency of the rotary oil pump in this pressure range.

In period 2, the amount of gas evolved depends upon the previous history of the calcine. The original removal of CO_2 during calcination, the reactivity of the product, and the opportunities for moisture and carbon dioxide adsorption offered by subsequent handling and preheating procedure, all play their part. Even under ideal conditions, the pumping system must remove

manded, since no gas is evolved and magnesium vapor will remove oxygen and nitrogen. Practically, however, these systems are not absolutely gastight, and a reasonable pumping speed is required.

The choice of suitable commercial pumps for these tasks presented some difficulties. It was decided that the pilot plant should employ only equipment that could be obtained on the North American market with immediate delivery, since a prime purpose of this work was to develop

a method applicable during the war. Mechanical oil-sealed rotary pumps of rugged design were available, which would serve during the first and second "periods."

Fig. 8, taken from the Leybold catalogue No. 27, shows the characteristics of the three types of pumps. Pressures of the order of 0.1 mm. are ideal for this process,

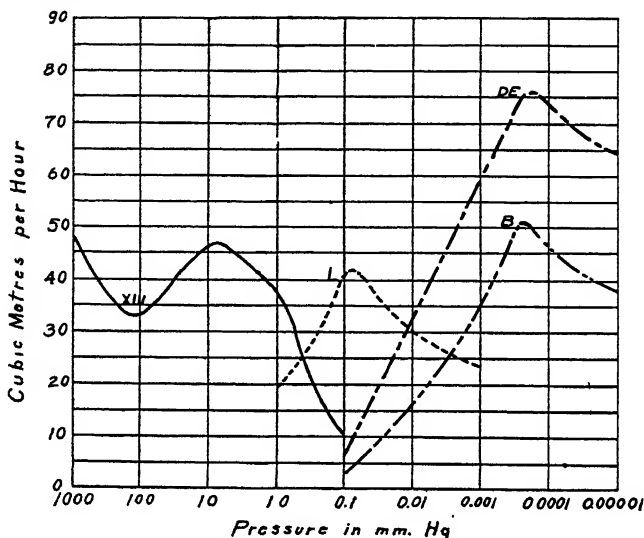


FIG. 8.—PUMPING SPEEDS OF VARIOUS TYPES OF PUMPS.
(From Leybold catalogue 27.)
XIII. Mechanical pump.
L. Jet pump.
DE and B. Diffusion pump.

These pumps are not well suited for the third "period," owing to their loss in volumetric efficiency at pressures below 0.1 mm. Owing to the unavailability of satisfactory commercial pumps for "period" 3 (Fig. 7) it was decided to use oversize mechanical pumps, so that a reasonable pumping rate would be available during the "holding" period.

Actually the ideal pumps for this service were known and described in the technical literature and commercial models were on the market in Europe. Smaller sizes were employed in all the laboratory work of this research. These pumps utilize the jet* principle with or without the well-known diffusion principle.

*The term "jet pump" is employed as applied by Leybold. It refers to a special type of diffusion pump, which will operate in the range 0.001 and 10 mm. Hg. These pumps were recommended by Leybold for melting metals in vacuo.

and the speed of the jet type of pump is at a maximum in this range. The diffusion pump alone gives little assistance in this range, since it will not operate until the pressure in the system is below perhaps 0.2 millimeter.

Mechanical pumps that will reduce the pressure in the retorts to the order of 0.2 mm. at a satisfactory speed will necessarily be so large as to be able to attain the requisite ultimate pressures of 0.150 mm. a short time thereafter. In other words, the greater part of the gas evolution has taken place when the pressure has been reduced to 0.200 mm. Hence, the addition of diffusion pumps operating at and below this pressure seemed unnecessary.

The pumps used in this pilot plant and subsequently in the first commercial plant were of the oil-sealed rotary type, capable

of reaching ultimate pressures of 0.01 to 0.05 mm. Hg. Jet pumps, which would have operated against a backing pressure of 1 to 2 mm. and with high pumping

provided, one with a dust filter for the initial drawdown, and one for holding. By this arrangement, the gross contamination of both pumps by water was

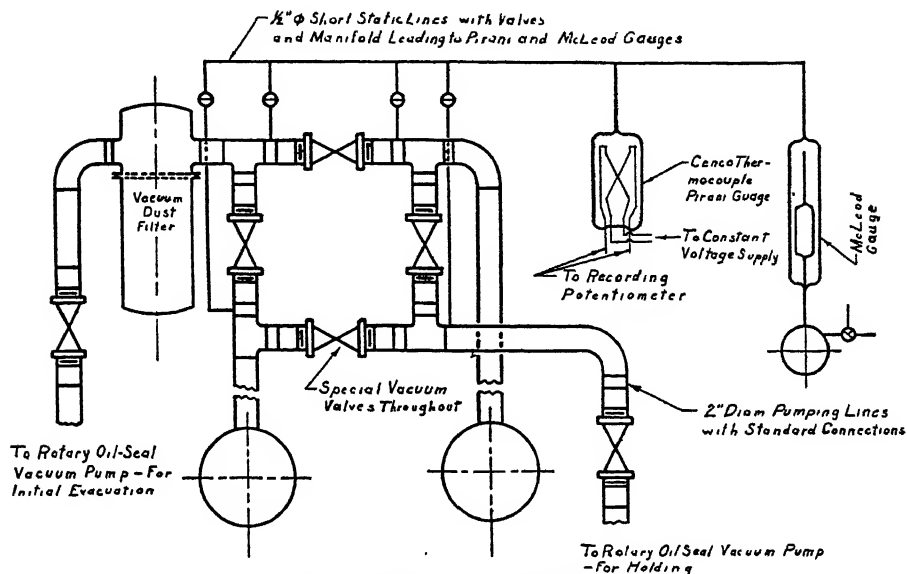


FIG. 9.—PILOT-PLANT VACUUM SYSTEM.

speeds in the range 1.5 to 0.050 mm., would have been employed if available. Such pumps have been placed on the American market since the first design of the pumping system was made in November 1941. (Pumps for the Canadian commercial plant were purchased on Dec. 3, 1941.)

Water accumulates in the pump oil and must be removed in order to maintain low pressures. Three methods were examined: (1) removal of water by centrifuging, (2) removal of water and other volatile liquids by heating in vacuo as well as filtering and de-acidifying the oil, (3) removal of water and volatile liquids by vaporizing at atmospheric pressure.

Method 2 gave oil of low vapor pressure and was adopted for full-scale plant operation.

The basic vacuum system of the pilot plant is shown in Fig. 9. Two pumps are

avoided. The vacuum lines were of large size, 2 to 3 in., as called for by theory when high pumping speeds at low pressure are desired.

The valves used in the vacuum lines were of the packingless type, the closure being effected by a rubber gasket and seating. These valves were found to be subject to cross leaks, presumably due to dirt that worked in under the rubber gasket. Pressure-lubricated plug valves were used in later work and found satisfactory when properly serviced.

The vacuum lines were partly streamline copper tubing and partly ordinary threaded joints painted with Glyptal. The 2-in. vacuum line was welded to the retort in later designs and carried through a flexible reinforced rubber tube in early designs, as shown in Figs. 2, 3 and 4.

The retort itself was closed by a mild-steel plate. The early designs (Figs. 2

and 3) were provided with a rubber gasket about 2 in. wide, cemented to the cover. The final closure is illustrated in Fig. 4, where the seal was made by a molded gasket, fitted in a machined groove in the head, pressing against a corresponding machined ridge on the flange of the retort. The head was provided with lugs so that it could be hung on the retort until the vacuum was applied when it was held sufficiently firmly by atmospheric pressure.

The McLeod gauge was employed for measuring pressures. It was felt, however, that a more rugged and preferably a continuous method should be provided. A very satisfactory device was found in the thermocouple-type Pirani gauge. The pilot plant from the first employed such a gauge, supplied by the Central Scientific Co. Five hundred millivolts across the hot wire gave thermocouple outputs up to 15 mv. at 0.001 mm. Hg. The calibration changed with the composition of gas in the gauge. This changes from air to hydrogen and argon as the experiment proceeds, owing to the reaction between magnesium and all oxidizing gases. This simple, hot-wire gauge was very useful and its use in the commercial plants was recommended by the authors.

The vacuum system designed by the authors for the commercial plant followed the same general arrangement. Four retorts were treated as an operating unit and were connected to a common manifold. Each group was piped (3-in. lines) to a 100-cu. ft. holding pump, which was placed as close as possible. Five such units were piped to a common pulldown pump. Both sets of pumps could be isolated with valves, while an emergency valve was placed over each retort.

If a jet-type mercury or oil-vapor pump working against backing pressures of 1 to 3 mm. Hg had been available, it would have been possible to arrange the five groups of four with a common mechanical backing pump, each group being

evacuated by a vapor pump. If high-speed vapor pumps become available, it will be possible to hold 20 or more retorts with a single pump. In all these multiple arrangements the operating cycle must be considered, since every time a freshly charged group is thrown into the system a fresh mass of gas must be removed. The original grouping coped with this situation by isolation of units.

FLOWSHEET AND PREPARATION OF RAW MATERIALS

All the steps in the pilot-plant operation are represented in the flowsheet of Fig. 10.

Crushing and Calcination

Most experiments employed a coarsely crystalline dolomite from quarries at Portage du Fort, Quebec, and from the Gould quarry, Renfrew County, Ontario. The rock was so uniform in chemical composition that no special sorting, blending or mixing operations were necessary.⁸ Numerous samples of rock from other quarries were tested and precautions were taken when necessary to secure uniform samples. The lumps of dolomite as obtained from the quarry were crushed in a gyratory crusher with an opening of $\frac{3}{4}$ in. The product was screened to three fractions, which were calcined separately. These sizes were $-\frac{3}{4} + \frac{1}{4}$ in., $-\frac{1}{4}$ -in. +8 mesh and -8 mesh. This sizing was necessitated by the friable nature of these crystalline dolomites, which produce a wide range of particle sizes and make a very undesirable feed for a rotary kiln because of the close packed mass formed.

The dolomite was calcined in a small rotary oil-fired kiln.* The internal diameter of the cold end was 14 in. for the first 12 ft., then it increased uniformly to 30 in. in the next 4 ft. The "hot" zone was 30 in. in diameter and 6 ft. long,

* The calcination procedure followed the recommendations of M. F. Goudge of the Bureau of Mines Laboratories, Ottawa.

making an over-all kiln length of 22 ft. The lining was good quality firebrick 6 in. thick in the hot zone and $4\frac{1}{2}$ in. thick at the cooler end. The kiln was run at 3

Raymond hammer mill or a set of rolls. Find grinding was done in a Raymond impact mill. When finer grinding and more uniform particle size were desired, a Gayco

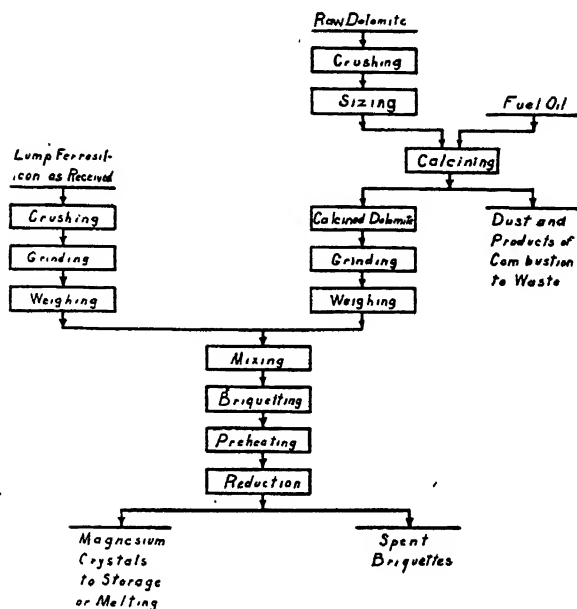


FIG. 10.—FLOWSHEET, REDUCTION OF DOLOMITE BY FERROSILICON.

r.p.m. With the usual feed rate of 100 lb. rock per hour, it is estimated that $2\frac{1}{2}$ to 3 hr. was required to pass through the kiln, with only about $\frac{1}{2}$ hr. in the cooler or narrower end. Calcination conditions could be held reasonably constant with the controls available and a calcine with uniform and desirable properties could be produced. The calcine was discharged from the hot end of the kiln at a dull red heat and was allowed to cool in air for some time before being stored in closed iron drums. The coarsely crystalline dolomites were considerably reduced in size during the calcination, especially the larger feed sizes, but the product was not entirely reduced to natural crystal sizes.

Calcine and Ferrosilicon Grinding

The calcine was crushed to approximately 8 mesh by one pass through a small

air separator was placed in series. The air separator removed the fines from the mill product by flotation in air, which was constantly recirculated, thus minimizing hydration and recarbonation of the calcine. The oversize was returned to the mill for regrinding. The reduction in size could be varied widely by omission of the finer grinding steps and by adjustments in each machine.

The ferrosilicon was received in large lumps and was broken down somewhat by hand. It was then put through a jaw crusher and ground as fine as required by secondary grinders, such as a disk grinder or rolls. Sometimes the product was sized on vibrating screens; otherwise, it was put through a given screen and the rejects were returned to the grinder.

Weighing, Mixing and Briquetting

The ground calcine and ferrosilicon were weighed for mixing in batches of a total weight of about 125 lb. If a catalyst or other addition agent was being tried, it was added at this point. The various weighed ingredients were dumped into a "Day" ribbon-type mixer. The mixer was cleaned out after each batch had been blended. Although mixing was complete in about five minutes with this machine, a nominal 20 min. was allowed.

Briquetting is a vital step in the process. The blend from the mixer was therefore pressed into pellets or briquettes in various ways. The properties of the calcine determined the ease with which briquetting was accomplished. With some dolomites, predensification or precompression of the mix was required before satisfactorily coherent briquettes could be produced, and with others it was almost impossible to produce hard briquettes even after predensification. This operation and its dependence on the type of dolomite used is discussed further under Experimental Results. Precompression and briquetting were done in two machines—a rotary tablet machine and a Baldwin-Southwark piston press. The former was suitable either for making final pellets or for precompression only and produced briquettes up to a maximum of about $\frac{7}{8}$ -in. diameter by $\frac{3}{8}$ in. thick. It was used as a precompressor for the most part and not to make briquettes. The clogging and jamming of the punches due to the fine powder collecting on the bearing surfaces of the lower punch-guides gave trouble in the operation of this machine.

The Baldwin-Southwark machine was a single-punch 70-ton press, which produces a cylindrical pellet $\frac{1}{4}$ to $\frac{3}{4}$ in. thick by 2 in. in diameter. The thickness was under the control of the operator and usually the $\frac{1}{2}$ to $\frac{5}{8}$ -in. size was produced. The machine was designed for pressing much

coarser material but operated reasonably satisfactorily on a blend that was predensified or precompressed. The best results were obtained with a mixture of partly formed pellets and powder. This machine produced briquettes at the rate of about 10 per minute, or about 100 lb. per hour. It was fitted with independent guides for the punches, and therefore would operate successfully with a worn die. The punches became protected with a layer of hard powder and a long life was obtained.

Preheaters

The preheaters consisted of suitable lengths of 8-in. wrought-iron pipe heated electrically by Chromel winding. The ends were closed by loosely fitting thermally insulating plugs. These served to retain the charge, since the tubes were suspended at about a 30° angle, and reduced circulation of air through the charge. The temperature was manually controlled.

Operations of a Typical Experiment

The operations of typical runs in the 8-in. and 10-in. retorts are recorded below. The briquettes, prepared as previously described, were weighed, the minus 4-mesh dust and broken lumps were screened out and the residue was dumped into the preheater tube. In the course of about 4 hr., the preheater attained about 650°C. The briquettes were poured from the latter to a trough placed at the mouth of the retort. While still red hot, they were pushed in with an iron hoe. The 8-in. retort with a 5-ft. heated section held 65 to 70 lb. when packed, with about 1 in. space along the top of the tube and all the briquettes inside the hot wall of the furnace. The 10-in. retort held about 120 lb. under similar conditions. Cold charging was carried out in a similar manner, excluding the preheater.

The radiation shield was then set in position as shown in Figs. 2 or 3, the

condenser was pushed in, the condenser cover and baffles, together with the retort cover were fitted and the retort was evacuated. The operations of charging and closing the retort required about ten minutes. The accompanying page chosen at random from a Laboratory notebook shows the temperature and pressure cycles, together with the weight and composition of a charge for a typical run.

furnace was made after the natural-draft burners were installed and when a single charge of 65 lb. of briquettes was placed in the retort. The results, representing an average temperature cycle, are plotted in Fig. 11. The pressure cycle of run number 548S₂, which was chosen as typical, is plotted in Fig. 7.

With the 10-in. retort described, the temperature cycle was not as favorable,

October 26th, 1941 Shifts: 8 - 4 Operators: S.D.H.
4 -12 J.D.G.

Experiment No. 280F2 - Purpose - To test effect of thicker pellets.

Preheating: Charge Lot 214 - 4 lbs.
Lot 215 - 61 lbs. - 65 lbs.

Preheater charged at 9.00 a.m.
Maximum temperature 662°C.

Composition of charge - Mol Ratio 1.25 : 1::MgO:FeSi.
Dolomite - Portage du Fort Quarry.
Ferrosilicon - 79.2% Si, 90% - 200 mesh.

Retort charging begun 4.05 p. m.
Retort closed and evacuated 4.15 p.m.

TIME	TEMPERATURE		VACUUM		REMARKS
	THERMO- COUPLE	OPTICAL PYRO- METER	PULP	PRESS MM:HG	
30'	4.35 p.m.	1118°C	1118°C	Stokes	0.25 Capacitrol
60	5.05	1120	1120	"	.15 set at 1135°C
90	5.35	1121	1121	"	.11
120	6.05	1119	1121	"	.13
150	6.35	1121	1124	"	.12
180	7.05	1123	1125	"	.095
210	7.35	1122	1124	"	.092
240	8.05	1121	1125	"	.090
270	8.35	1120	1125	"	.091
300	9.05	1121	1121	"	.091
330	9.35	1121	1121	"	.110
360	10.05		1125	"	
390	10.35	1111	1125	"	.120
420	11.05	1127	1125	"	.102
450	11.35	1125	1126	"	.098
465	11.50				Tube Opened.

(1) Yield - 9.1 lb. Mg.

(2) Si Efficiency 80.5%

(3) Deposit Grade A.

COPY OF PAGES 12 AND 13 FROM N.R.C. LABORATORY NOTE BOOK NO. 541.

The optical pyrometer was taken as the standard or correct value in temperature observations. The thermocouple readings were those shown by a thermocouple in contact with the outside of the retort, while the Capacitrol setting shows the temperature in the furnace atmosphere by a thermocouple suspended from the roof.

A careful measurement of the temperature cycle of the 8-in. retort in the gas-fired

since this retort held a charge of about 120 lb. The pressure cycle, which is also shown in Fig. 7, was somewhat poorer, especially during the early part of the run. The ultimate pressure, however, was as low as with the smaller retort. This indicates the need for adequate pumping capacity during the "pulldown" period. After preheated briquettes had been charged, $\frac{1}{2}$ to $\frac{3}{4}$ hr. was required for

return to normal temperature. The pressure was reduced to 0.3 mm. in about one hour, and to 150 microns or less in the next half hour. In other respects the runs

processing establishment, a single melting would be sufficient to produce alloys and castings. In the laboratory, some melting tests, carried out by the established open-

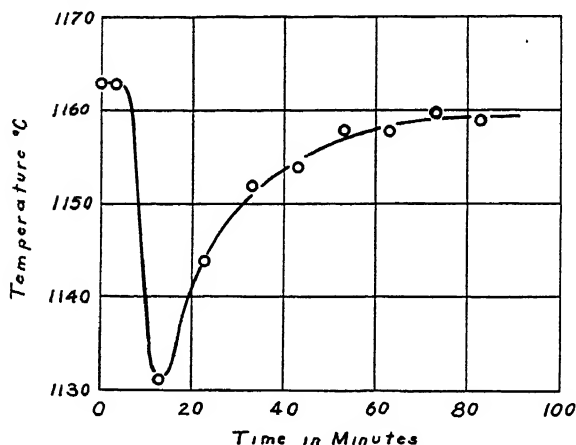


FIG. 11.—TYPICAL TEMPERATURE CYCLE, 8-INCH RETORT.

with the 10-in. retort were similar to those in the 8-in. retort.

At the end of the heating period, the vacuum is broken and the closure removed. With a satisfactory vacuum cycle minor sodium fires may occur spontaneously on the baffles without igniting the massive metal deposit. If condensing conditions have been properly adjusted, a coherent "crown" of magnesium is produced, as illustrated in Fig. 12. After the removal of the baffles, the condenser is removed. The condensate is pressed from the condenser tube by a hydraulic press or similar device. Split condensers were tried for a time but were not adopted in Canadian plant practice.

The crystal metal is contaminated only by small percentages of other metals with a very low vapor pressure at the reaction temperature, mainly calcium and silicon. Typical analyses are given in Table 2. The crowns may be melted directly to remove oxide and cast into ingots for marketing.

Of course, if the process is operated in conjunction with a foundry or other

pot method with $MgCl_2$, KCl , $NaCl$ fluxes, indicated that a melting loss of 3.5 per cent on crystal metal was readily obtainable.

The briquettes retain their shape during reaction and therefore must be removed

TABLE 2.—Purity of Magnesium

Constituent	Commercial Electrolytic ^a	Distilled Magnesium ^a	Retort Process, Crystal Magnesium
Fe	0.030	<0.001	0.002
Ni	<0.0005	<0.0001	<0.001
Cu	<0.005	<0.0001	0.002
Si	0.004	<0.001	0.003
Al	0.01	<0.001	<0.007
Mn	0.002	<0.0005	<0.001
Na	<0.005	0.002	<0.0005

^a From Hanawalt et al.¹

as such at the end of a cycle. The composition after reaction is dicalcium silicate, free lime and magnesia and low-grade ferrosilicon. While cooling in air, the iron and silicon oxidize to some extent and the crystal transformation of the dicalcium silicate from beta to gamma form, with a decrease in density, takes place with consequent disintegration of the briquettes.

This transformation may be delayed so that the briquette residue does not disintegrate for some time after cooling. Numerous uses for this product have been

feasible and should extend the possible field of application. It may also be possible to recover unreacted ferrosilicon from the residue.



FIG. 12.—SECTION OF A "CROWN" OF CRYSTAL MAGNESIUM.

suggested, such as cement filler, metallurgical slag ingredient, fertilizer. Recarbonation of the free lime may be

EXPERIMENTAL RESULTS

The gas-fired furnace was operated periodically and some 1500 individual ex-

periments were carried out in this apparatus alone. Except where indicated otherwise, all the work described in this paper was carried out prior to Aug. 1, 1942.

under favorable conditions. Early pilot-plant experiments were carried out therefore at 1120° to 1125°C. When it had been shown that satisfactory operation was

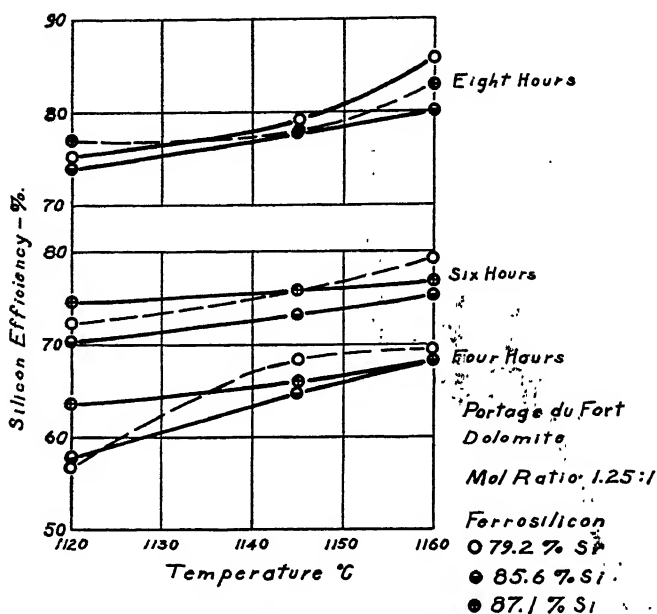


FIG. 13.—EFFECT OF TEMPERATURE.

During these experiments, the main variables influencing the reaction were examined. At the same time, information was obtained regarding the operation of the process, life of retorts, efficiency of silicon utilization and other vital commercial factors. The important factors in the reduction step are: (1) effect of retort temperature on reaction velocity; (2) effect of pressure; (3) size and shape of retort; (4) weight of charge per retort. The important variables inherent to the charge, such as quality of calcine, particle size, ferrosilicon composition and briquette size and density, were held as constant as possible while the variables were examined.

Temperature of Reaction

Previous work had shown that the reaction will proceed rapidly at 1100°C.

possible under these conditions, the temperature was successively raised to 1145° to 1150° and 1160° to 1165°C., the object being to operate at the highest temperature compatible with good retort life. Curves of silicon efficiency versus temperature are plotted in Fig. 13 for three grades of ferrosilicon mixed with excess calcined dolomite. The convention of referring first to the dolomite in statements of mol ratios has been adopted in this paper.

The curves show a definite increase in silicon efficiency with increasing temperature, although the slope is small. The temperature coefficient of the reaction is roughly the same for each reaction time.

Since ferrosilicon is by far the more expensive reactant, yields or "silicon efficiencies" are calculated as follows: Si eff.

$$= \frac{\text{Mg (collected)}}{\text{Mg equivalent of silicon present}} \times 100$$

This practice is retained even when silicon is present in excess.

Rate of Reaction

The rate of reaction depends, among other factors, on the temperature and on the flow of heat to the reactants. Thus,

temperatures are somewhat steeper, as might be predicted from the higher rate of reaction at the higher temperatures. The range of time is somewhat extended in Fig. 15 and shows the rapid falling off under 4 hr. and the slow increase above 8 hr. as mentioned above.

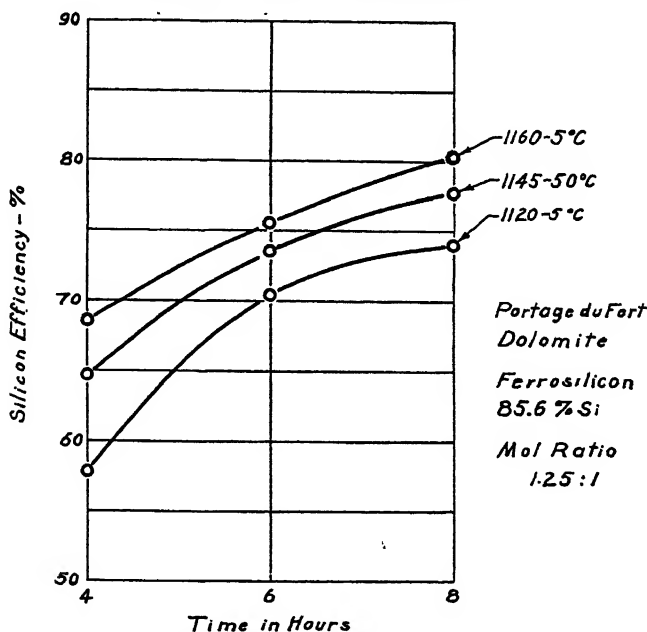


FIG. 14.—REACTION RATE AT VARIOUS TEMPERATURES.

while the experiments in the 4-in. retort showed very little increase in yield after 3 hr., those in the 8-in. retorts required 8 hr. or more to reach the same efficiency of reaction, owing to slower penetration of heat.

After a few exploratory experiments, the time range of 4 to 8 hr. was found to be the most informative and was adopted in most of the work with 8-in. retorts. Increase of the time beyond 8 hr. resulted in relatively small increases in yield, while times less than 4 hr. gave very low and irregular yields. In fact, the runs at 4 hr. were generally more irregular than the 6 and 8-hr. runs. Typical time curves are shown in Fig. 14 for the three temperatures mentioned. The curves at the lower

It is realized, of course, that in commercial continuous operation of the retort, the choice of a reaction time will be made in the light of economic factors and the reaction-rate curve for the particular size of retort employed. The following calculations from the data of Fig. 15 show the metal produced in a 24-hr. period, assuming 100-lb. charges that are reacted for 4, 6, or 8 hr.:

Cycle Time, Hr.	Silicon Efficiency, Per Cent	Number of 100-lb. Charges per 24 Hr.	Mg Produced per 24 Hr.
4	65	6	66.0
6	77	4	52.2
8	80	3	40.7

The highest output with lowest silicon efficiency is achieved with the 4-hr. cycles. Only the plant operator can make the choice, since he alone can balance oper-

in the 6 and 8-hr. runs in the 8-in. retort. The reasons for desiring pressures of the order of 0.1 mm. Hg are connected almost solely with the nature of the deposit.

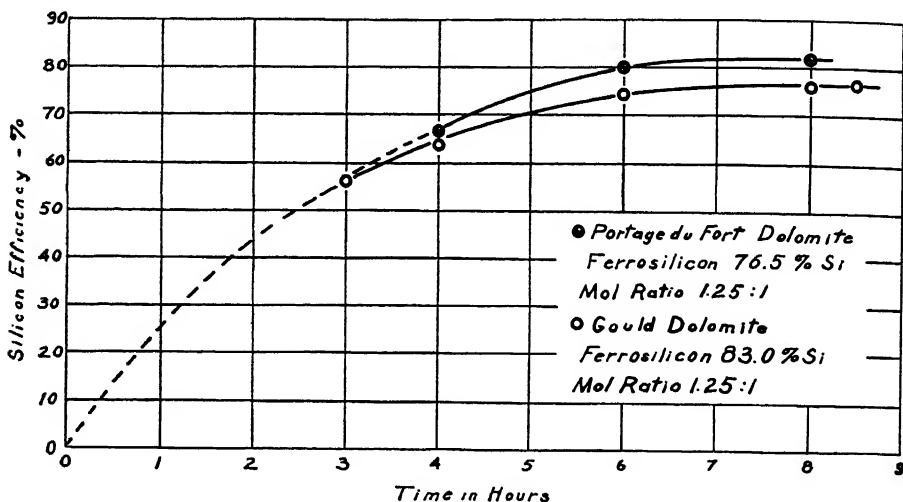


FIG. 15.—RATE OF REACTION AT 1160°C.

ating costs against silicon costs. As a preliminary suggestion, 6-hr. cycles were considered the optimum for 8-in. retorts and 8-hr. cycles for 10-in. retorts. The maximum ease of operation follows the use of the longest feasible cycle. The burden on the vacuum system is reduced and lower melting losses are incurred with the large "crowns."

The Vacuum Cycle

The main effects of the vacuum cycle have already been described. Below some minimum, pressure chiefly influences the quality or denseness of the deposited magnesium and the separation of sodium.

As far as the effect on the weight of metal produced is concerned, no relation could be found. If the pressures were not reduced below 0.5 to 0.7 mm. during the greater part of the run, so much powder and loose crystals were produced that loss of the yield by fire usually resulted.

Between 0.5 and 0.002 mm., no difference in weight of yield has been observed

With low pressures, the deposit invariably is dense, and the "crowns" are easily removed from the furnace and subsequently show low melting loss.

Weight of Charge per Retort

For a given retort, it was generally found that reduction in the size of charge below that required to fill the section of the retort inside the furnace wall had no effect on the silicon efficiency (assuming equal packing of the charge). In the short 8-in. retorts used in these experiments a 65-lb. charge of Baldwin-Southwark pills filled the retort to within 12 in. of the condenser section. The effect of increasing or decreasing the length of charge is shown in Table 3. As would be anticipated, the yield falls off as the weight of charge is increased, especially at the shorter reaction time.

This is due largely to the placing of part of the charge in the cooler mouth of the retort, since the charging practice was

uniform in other respects, such as tightness of packing into the retort.

A small channel remains along the top of the charge, since it is almost impossible to

comparison of yields versus time curves is shown in Fig. 16.

In general, it may be concluded that the reaction times, 6, 7½ and 9 hr. with the

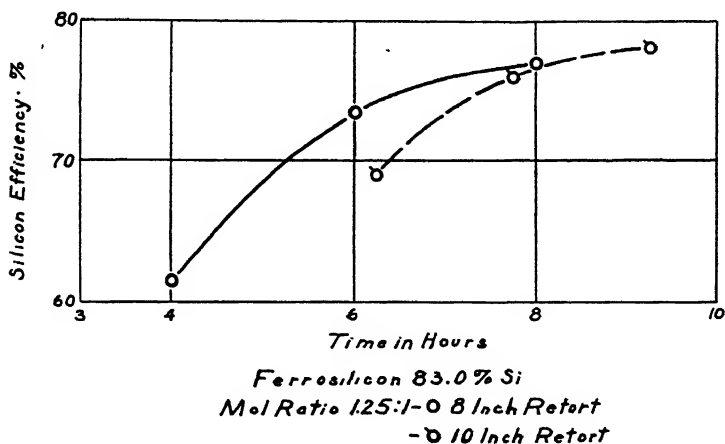


FIG. 16.—EFFICIENCIES OF 8 AND 10-INCH RETORTS.

pack a horizontal retort. This channel probably is advantageous, since the magnesium vapor then never travels a distance greater than the diameter of the retort

TABLE 3.—*Effect of Increasing or Decreasing Length of Charge*

Temperature, 1120–5°C.

Portage du Fort dolomite.

Ferrosilicon 85.6 per cent Si, minus 200 mesh.

Mol ratio 1.25:1.

Wt. of Charge, Lb.	Silicon Efficiency		
	4 Hr.	6 Hr.	8 Hr.
50	66	70.5	75.0
65	58.0	69	74
75	53	68	65

before leaving the briquette mass. A simple calculation of vapor velocity gives surprisingly high values, and emphasizes the advantages of a free vapor passage.

Size of Retort

A series of runs was done in the 10-in. retort with the same raw materials as used in some of the 8-in. experiments. A

10-in. retort corresponded fairly closely with the times 4, 6 and 8 hr. with the 8-in. retort.

Assuming that 6-hr. cycles with an 8-in. retort and 8-hr. cycles with a 10-in. retort give equal silicon efficiencies, the 24-hr. production of 10-in. retorts is $(10\frac{3}{4} \times \frac{3}{4}) = 1.17$ times that of 8-in. retorts. Thus, production is greater and the amount of labor is reduced when the larger retorts are employed.

Composition and Crystal Structure of the Dolomite

When the reduction step variables discussed in the foregoing pages are held constant, the effects of the various factors in the production of the briquetted charge can be investigated. Important among these are the chemical composition and crystalline nature of the raw dolomite.

Many samples of dolomite, of varying compositions, were tested in the pilot plant, while a large number of others were analyzed and tried out on a laboratory scale. The compositions of those used in

the pilot-plant experiments are given in Table 4. The lime and magnesia contents varied rather widely, as well as the percentages of insoluble and of trivalent oxides. Of the dolomites listed, only the following are of the macro or larger crystalline varieties: Portage du Fort, Quebec; Gould, Renfrew, Ont.; New Canaan, Conn.; Wheatland, Wyo.; and

dolomites varied widely. In addition to the controllable factors such as calcinations and grinding, the nature of the dolomite itself exerted an important effect. It was observed that microcrystalline dolomites gave more trouble in this operation than the macrocrystalline varieties.

A number of the samples whose analyses are listed in Table 4, and which showed

TABLE 4.—*Compositions of Dolomites and Calcined Dolomites Tested in Pilot Plant*
PER CENT

Origin of Sample	MgO	CaO	Insoluble	R ₂ O ₃	Loss on Ignition	Remarks
Gould quarry, Renfrew Co., Ont.	21.04 (MgCO ₃) (44.00)	31.28 (CaCO ₃) (55.82)	0.20	0.10		At present being used in full-scale plant operation
Portage du Fort, Quebec.....	43.92	55.88	0.32	0.24		
Nat. Lead Co. A, Sudduth, Texas.....	38.2	55.2	3.6	0.7	2.3	Sample 1
C. Flat Creek, Tenn.....	36.7	54.6	6.3	1.6	0.8	Sample 2
D, Dolcito, Ala.....	34.6	55.4	7.0	2.6	0.4	
J, Dolcito, Ala.....	34.1	50.4	14.1	0.7	0.7	
	20.6	30.8	1.75	0.35	46.5	Raw rock
	38.5	57.6	3.3	0.65		Calculated from raw rock analysis
G. K. L, Fostoria* and Gibsonburg, Ohio	Analyses similar to M and N below					
M, Luckey, Ohio.....	41.3	57.2	0.3	0.2	1.0	At present being used in full-scale plant operation
N, Luckey, Ohio.....	41.1	57.4	0.3	0.4	0.8	At present being used in full-scale plant operation
Hespeler, Ont.....	41.0	57.8	0.7	0.5		
Standard Lime and Stone Co., Millville, W. Va.	22.18	30.03	0.75	0.82	46.14	
	41.1	55.7	1.39	1.52		Calculated from raw rock analysis
Nat. Gypsum Co., Luckey, Ohio.....	40.1	56.0	1.1	0.7	2.1	
	19.9	31.5	0.21	0.24	47.3	
New England Lime Co., New Canaan Conn.	39.6	58.5	0.45	0.45	0.78	
	38.9	57.8	1.8	0.9	0.6	
Nichols Engineering Co., New York...	37.8	57.8	3.0	1.1	0.3	
	38.7	55.4	4.7	0.7	0.5	
Warner Co., Cedar Hollow.....	40.4	57.1	1.4	0.5	0.6	
Wheatland, Wyo.....	33.4	51.4	7.8	1.6	5.8	
Wingdale, N. Y.....	37.4	55.6	2.4	2.0	2.6	
	39.8	55.2	1.2	0.6	3.2	Check analyses of same lot
	37.9	57.7	1.3	0.8	2.3	Second lot
New Jersey Zinc Co.....	21.3	30.9	1.1	0.5	46.2	
	39.6	57.43	2.04	0.93		Calculated from first analysis

Wingdale, N. Y. The remaining samples were of the microcrystalline variety. The large crystal size of the macrocrystalline dolomites involves special precautions in crushing and calcining, since they tend to break down to the natural grain size and will do so in the kiln if the feed contains coarse particles. Hence, calcination of the small sizes is essential if the rejection of a large fraction of the raw rock is to be avoided.

The ease of briquetting of calcined

wide variation in insoluble content, were reacted under identical conditions of time, temperature, mol ratio, and other factors. With the piston press, hard, well-formed briquettes were made in all cases. The results of some of these tests are shown in Fig. 17, where silicon efficiency and percentage of insoluble in the calcined rock are plotted, and an approximate curve is drawn. It would appear from these results that the insoluble or silica in the calcine acts merely as a diluent when present in

quantities up to about 3 per cent, while contents above this value notably depress the yields.

A point that probably is important in

However, advantage was taken of the greater vapor pressures of the alkali metals to achieve a separation from magnesium by means of the baffle arrangement placed

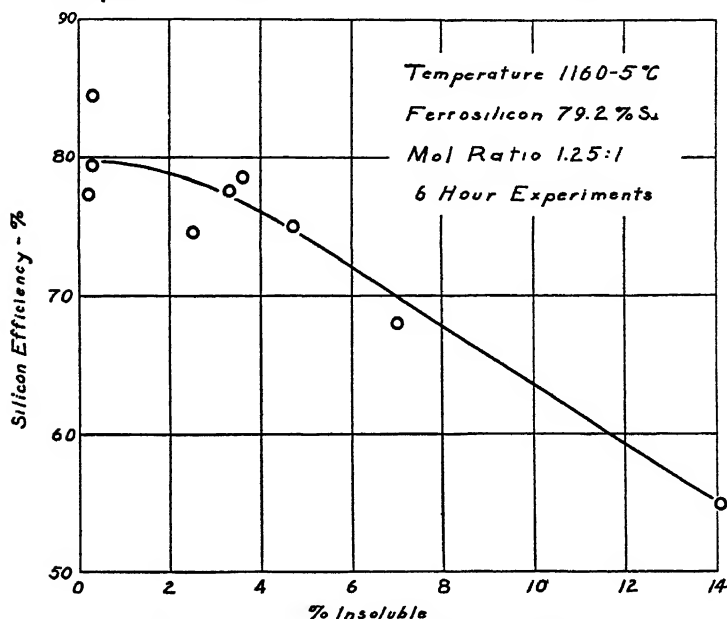


FIG. 17.—EFFECT OF INSOLUBLE IN DOLOMITE.

this connection is the distribution of the insoluble material, which consists in most cases of silica or magnesium silicates. If the silica is present as relatively large aggregations of quartz or silicates, it should solely have the effect of an inert diluent, while if it is widely dispersed, it would be expected to exert a greater depressing effect on the reactivity of the calcine.

Alkali Metals in the Dolomite

The presence of alkali metals is an important property of the raw rock as far as recovery of magnesium is concerned. The compounds of sodium and potassium apparently are not volatilized to any large extent on calcination of the rock, but are reduced in the reaction and condense with the magnesium metal. This presented one of the major problems of this process.

in the path of the magnesium and alkali-metal vapors. It was found from the full-scale pilot-plant experiments that a raw rock containing up to 0.05 per cent alkali metals would be readily handled with these precautions, assuming correct condenser temperature and provided a "satisfactory" vacuum cycle was obtained. By this is meant a vacuum cycle in which the pressure in the system was as low as 0.175 mm. for approximately the latter 75 per cent of the cycle.

When the amount of alkali metals in the rock increased to about 0.15 per cent, considerable difficulty was experienced in preventing the burning of the magnesium condensate due to incomplete separation of the sodium. It was found that the maintenance of a vacuum of 0.050 mm. Hg, or preferably lower, permitted the separation of the alkalis, when they were

present in the higher concentrations. It was noted that distinctly poorer deposits of metal were obtained with calcine high in sodium when other conditions in the system were identical. Experiments of this type were carried out in the two-retort furnace so that the temperature and pressure cycles were identical. A hotter condenser is required for high alkali contents.

Calcination of Raw Rock

The following factors in calcination were investigated:

1. Type of kiln—rotary, stack and Herreshoff.

Table 5, where the results of experiments with rotary versus stack and Herreshoff kilns are presented. No particular type of calcination apparatus can be stated to be definitely superior as far as silicon efficiencies are concerned. Samples calcined outside the laboratory were obtained by the courtesy of the various companies referred to in the first column.

In the same table, the results of a few experiments on soft versus hard burning are included. Samples supplied by The New England Lime Co. showed no real difference in this respect while samples from the Standard Lime and Stone Co.

TABLE 5.—*Effect of Calcination Procedure on Silicon Efficiency*

Mol ratio, 1.25:1.

Reaction temperature, 1160° to 1165°C.

Ferrosilicon ground to minus 65-mesh.

Source of Dolomite	Calcination Procedure	Si in FeSi, Per Cent	Silicon Efficiency			Remarks
			4 Hr.	6 Hr.	8 Hr.	
National Gypsum Co., Luckey, Ohio.	Stack kiln	78.5		71, 76		Two 6-hr. runs
National Gypsum Co., Luckey, Ohio.	Pilot-plant rotary kiln	78.5		70, 78		Two 6-hr. runs
	Stack kiln	78.5	50, 63	80, 77	81, 81	Ground at source
	Stack kiln	78.5	60	75	78	Ground at pilot plant
	Pilot-plant rotary kiln	78.5		81	82	Ground at pilot plant
New England Lime Co., Canaan, Conn.	Herreshoff kiln	79.2		75	81	
		79.2		74	79	Soft-burned sample
New England Lime Co., Canaan, Conn.	Rotary kiln at Canaan	75.4	64	75	78	Soft-burned sample
New England Lime Co., Canaan, Conn.	Rotary kiln at Canaan	79.2		75	76	Hard-burned sample
New England Lime Co., Canaan, Conn.	Rotary kiln at Canaan	75.4	61	75	78	Soft-burned; NaCl added to raw rock
New England Lime Co., Canaan, Conn.	Rotary kiln at Canaan	75.4		64	70	Hard-burned; NaCl added to raw rock
Standard Lime and Stone Co., Millville, W. Va.		79.2		71	73	Soft-burned sample
		79.2	61	74	77	Hard-burned sample

2. Type of burn (or temperature of calcination)—soft, normal and hard burn.

3. Addition agents during calcination.

The greater part of the calcine for these experiments was obtained from sources outside the pilot plant, since here only the small oil-fired rotary kiln described under Apparatus was available. Small lots of 500 to 1000 lb. produced under special conditions were supplied by producers with these special facilities.

Tests made to determine the possible effects of the type of kiln are shown in

indicated some advantage in using hard-burned calcine. These few results would suggest that little if any advantage results from either hard or soft burn. Again the effect of burning on briquette strength is excluded.

A few experiments on calcine produced from raw rock to which 0.25 per cent sodium chloride had been added are also included in Table 5. The soft-burned sample showed no effect from this addition while the hard-burned sample gave a lower

recovery of metal than that from any of the other methods of burning.

As will be evident from the foregoing, only preliminary investigations of the effects of calcination were included in this work, since the primary purpose of the experiments was to produce metal efficiently, and little effect seemed to result from the few gross variations of calcination procedure that were made. No experiments were carried out with calcine produced in coal-fired rotary kilns.

Composition of Ferrosilicon

The effect of the concentration of silicon in the ferrosilicon is an important factor in the efficiency of the reduction. In earlier work, it had been shown that ferrosilicon with silicon contents below 70 per cent was definitely less reactive. Commercial grades of ferrosilicon higher than 70 per cent include the 75, the 85 and the 90 per cent grades, all of which were examined.

A summary of arithmetical averages of various experiments on these grades of ferrosilicon is presented in Table 6. The results of runs under identical conditions are grouped together. The first general conclusion is that the high-silicon grade (96.2 per cent Si) is superior, especially at the lower temperature of reaction, and at the shorter times at the higher temperature. With the exception of the runs at 1120° to 1125°C., no other very distinct regularities or trends with changing silicon percentages are visible. In the runs at 1120° to 1125°C. in group 3 of the table, a distinct trend toward lower yields at the lower silicon contents is apparent. Lots of the same nominal composition frequently behaved differently. Minor impurities may play a part in the mechanism of silicon diffusion through the alloy.

A gross variation in the amounts of impurities in the ferrosilicon was made by using the "sweepings" material from nominal 75 and 85 per cent grades of ferrosilicon. These consist of chippings

from the outside of the ferrosilicon casting and contain much larger amounts of slag, sand, and other impurities than the normal grade. When these "sweepings" were

TABLE 6.—*Ferrosilicon Composition*

FeSi Per Cent Si	4 Hr.	6 Hr.	8 Hr.	Remarks
Portage du Fort dolomite. Mol ratio 1½:1. Temperature, 1160° to 1165°C.				
96.2	74.5	81	85.5	Single run at each time
85.6	68.4	75.5	80.3	
79.2	69.4	79.4	86.0	8 hr. is average of three runs
76.5	66.5	79.7	81.2	
72.4	58	68.5	71*	*Single-run; "sweepings"
68.2		63.3	64*	*Single-run; "sweepings"
Portage du Fort dolomite. Mol ratio 1½:1. Temperature, 1145° to 1150°C.				
87.1	66.4	76.0	78.0	
85.6	64.6	73.4	77.8	
79.2	68.4	75.9	79.2	
77.2	67	79	83	4 hr. and 8 hr. are single runs, 2 at 6 hr.
76.5	59.2	74.3	80.0	
72.4	56.0	67.0	68.7	"Sweepings"
68.2	50.5	61.5	63.5	"Sweepings"
Portage du Fort dolomite. Mol ratio 1½:1. Temperature, 1120° to 1125°C.				
96.2	55	77	73	Single runs
87.1	63.6	75.7	77.0	
85.6	57.9	70.2	74.0	
79.2	57.5	72.8	75.3	
Gould dolomite. Mol ratio 1.15:1. Temperature, 1160° to 1165°C.				
83.0	61.3	71.3	76.1	
79.2	64.0	73.0	76.4	
78.5	62.5	74.0	76.0	
75.4*	65.5	67.3	77.5	
Gould dolomite. Mol ratio 1.10:1. Temperature, 1160° to 1165°C.				
83.0	62.7	72.7	75.3	Three runs at each time
75.7*	56.6	66.7	72.2	
75.4*	61.1	72.7	76.3	

* Work done since Aug. 1, 1942.

tried in the reaction under otherwise normal conditions, the silicon efficiency fell off markedly. It may then be safely concluded that abnormally high con-

tamination of the ferrosilicon will cause a decrease in the yield of magnesium beyond that to be expected on the basis of mere dilution of the ferrosilicon by the impurities.

If 50 per cent ferrosilicon is ruled out on grounds of low reaction rate, 95 per cent FeSi is ruled out on grounds of cost. A choice must be made between 75 and 85 per cent. Numerous pilot-plant experiments in this range failed to justify the extra cost of the 85 per cent grade. The specification recommended called for 75 per cent plus. Most of the samples were of the order of 77 per cent. As with many other factors, the plant operator will choose the ferrosilicon grade giving lowest over-all costs.

It is important that the ferrosilicon be of uniform grade, since, as far as the reaction goes, the presence of 50 per cent FeSi is not compensated for by the presence or equivalent amount of the 85 per cent grade. No extensive analytical work was done during the period described by this paper, to establish the uniformity of sample shipments. Analyses usually were conducted on the ground sample, which was, of course, thoroughly mixed.

Particle Sizes of Reactants and Catalysts

Since the reactants are solids, it is reasonable to expect higher reaction rates the more finely the ingredients are ground. Whether the reaction is a solid-solid reaction where intimate reactant particle contact is presumably essential, or the more volatile reactant silicon produces a vapor which attacks the calcine, a small particle size would appear essential. The distance the Si atoms must travel to reach the surface of the FeSi particle would also be reduced by very fine grinding. Experiments were begun therefore with reactants in a superfine condition.

Ferrosilicon.—It was quite surprising when, at a very early stage of the work, it was found that a slightly higher yield was obtained when somewhat coarser ferro-

silicon was used, as indicated in the first part of Table 7. These differences in yields might well be taken as within experimental error and the preliminary conclusion drawn that in the range investigated no importance need be attached to the screen analysis of the ferrosilicon.

TABLE 7.—*Effect of Particle Size of Ferrosilicon*

Mol Ratio	Si in FeSi, Per Cent	Mesh	Silicon Efficiency, Per Cent		
			4 Hr.	6 Hr.	8 Hr.
Portage du Fort, Quebec, dolomite. Reaction temperature, 1145° to 1150°C.					
1.25:1	87.1	—65+100 —100+150 90 per cent —200	70 74 70	82 83 80	84 83 81
Gould dolomite. Temperature of reduction, 1160° to 1165°C.					
1.15:1	79.2	—6+10 —10+14 —14+20 —20+65 —65	58.7 62 67 62 65	56 74 78 79 74.5	71 75 80 77.5 79.5
1.25:1	83.0	—6+10 —10+14 —14+20 —20+65 —65	58.5 55.5 62 58 57	62 62.5 69 74 71	67.5 72.5 72 71.5 71

This conclusion is substantiated by the results of the later tests in which the range of ferrosilicon sizes was considerably extended. The results of single runs under each condition are plotted in Fig. 18. Characteristically, the 4-hr. runs are more irregular than those at longer times, but the results indicate an almost constant yield in the range investigated. Reduced yields with very fine Si are perhaps caused by superficial oxidation.

A more extensive range of large sizes of ferrosilicon was next tried, in order to establish the particle sizes at which the yield begins to fall off. The results of these experiments are shown in the latter part of Table 7, where it will be seen that the silicon efficiencies diminish above 14 mesh. This conclusion, of course, is restricted to these particular experimental conditions,

such as size of briquette, retort, grind of dolomite, etc.: For example, in a 2-in. retort with a reaction time of 30 min. the to a grind of all through a 65-mesh screen. The results of these tests are summarized in Table 8.

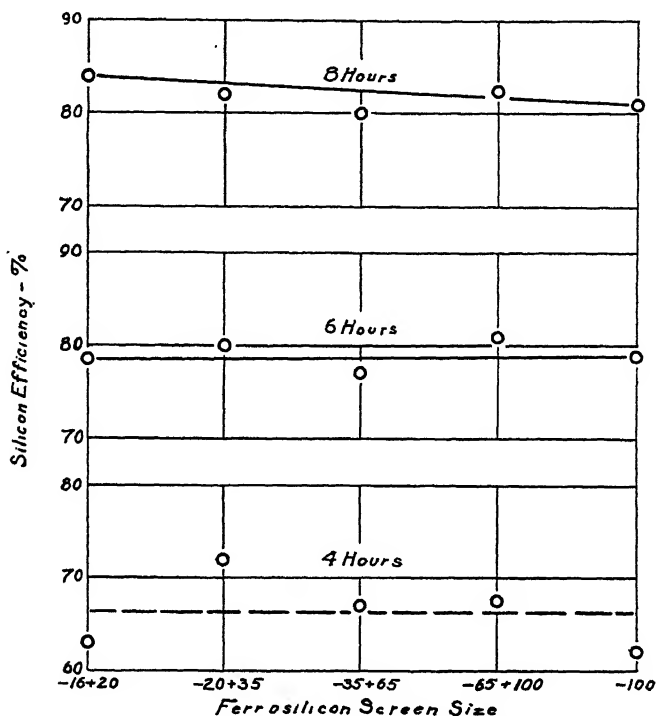


FIG. 18.—EFFECT OF FERROSILICON PARTICLE SIZE.

smallest particles used gave the highest yield.

With a view to approaching plant operating conditions, a grind where the ferrosilicon would all pass a 14-mesh screen was next compared with similar dolomite

Definitely higher yield was obtained with the finer grind in almost all instances. An increase of about 3 per cent is a rough mean.

Calcined Dolomite.—As with the ferrosilicon, it was first believed that the finest feasible grind of the calcine would be best. The first grinding system, therefore, included an air separator and a reduction to better than 98 per cent minus 200-mesh was obtained. When it was found that the ferrosilicon did not require fine grinding, coarser calcine was tried. The first coarse calcine used was the oversize or rejects from the air separator, which had the screen analysis shown in Table 9.

This material was first tested with the coarse ferrosilicon, -16+20 mesh, 76.5

TABLE 8.—Comparison of Ferrosilicon Sizes
Gould dolomite.
Temperature of reaction, 1160°–1165°C.

Mol Ratio	Si in FeSi Per Cent	Mesh	Silicon Efficiency Per Cent		
			4 Hr.	6 Hr.	8 Hr.
1.10:1	75.4	-14	57	72.5	72.5
		-65	61.1	72.7	76.3
		-14	61.5	69	72.5
1.15:1	75.4	-65	65.5	67.3	77.5
		-14	60.7	70.5	76.5
		-65	62.1	75.3	78.3
1.25:1	78.5	-14			
		-65			
		-14			

per cent Si at 1160° to 1165°C, and then with -65+100-mesh ferrosilicon with the results shown in Table 10.

TABLE 9.—*Screen Analyses of Ground Dolomite*

Mesh	Detail of Grinding				
	Air Separator Over-size or "Rejects," Portage du Fort Dolomite	Once through Raymond Impact Mill			Gould Dolomite. One pass through Raymond Hammer Mill— $\frac{1}{4}$ " Grate
		Portage du Fort Dolomite	Gould Dolomite		
			Sample 1	Sample 2	
+ 14					2.1
+ 20					5.7
+ 28					9.4
+ 35				1.2	14.4
+ 48				3.6	14.0
+ 65				6.6	12.3
+ 100	46	30	35	9.3	10.1
+ 150			15.8	15.2	9.2
+ 200	37	24	11.6	12.0	5.8
- 200	17	46	37.6	38.5	16.7

Comparison with the values in Fig. 18 indicates that even with the combination of two coarse reactants the yields were decreased only about 5 per cent, while with the finer ferrosilicon the results were as good as with both reactants finely ground. This then was taken as an indication that fine grinding of the calcine was also unnecessary provided the ferrosilicon was reasonably finely ground.

TABLE 10.—*Testing of Coarse Calcine*

Ferrosilicon Mesh	Silicon Efficiencies		
	4 Hr.	6 Hr.	8 Hr.
- 16+20	58		75
- 65+100	67, 61, 61	82, 72	81
- 100	61, 66	80	82, 77

These results permitted the abandoning of the air separator and use of calcine ground by a single pass through the Raymond impact mill. Resultant size distributions are shown in Table 9.

A further test was made with a coarser grind than the Gayco oversize described

above, which was produced by one pass through the Raymond hammer mill. Using the $\frac{1}{8}$ -in. grate in this mill, the size distribution indicated in Table 9 was produced.

This is a considerably coarser grind than even the air-separator rejects and was considered an upper limit for the process. The results of single tests at each time are given in Table 11, which includes the averages of a large number of runs with finer dolomite.

TABLE 11.—*Effects of Calcine and Ferrosilicon Particle Sizes*

Reaction Temperature, 1160°-1165°C.
Ferrosilicon, 78.5 per cent Si.
Mol Ratio, 1.25:1.

Calcine Grind	Ferrosilicon Grind	Silicon Efficiencies			Remarks
		4 Hr.	6 Hr.	8 Hr.	
Raymond hammer mill, $\frac{1}{8}$ -in. grate.....	- 14 mesh	62	67	74	Single runs
Raymond hammer mill, $\frac{1}{8}$ -in. grate.....	- 65 mesh	63	77	79	Single runs
Ray impact mill or finer	- 65 mesh	62	75	78	Averages

The coarse calcine grind shows a distinct falling off in yield when used with coarse ferrosilicon, but a slight advantage when mixed with finer ferrosilicon. Thus, the earlier results are confirmed; namely, that a falling off in yield occurs only when both reactants are coarse.

It was found that the coarser grind simplified the rather troublesome operation of briquetting. With the machines available, it had been necessary to precompress the mix before satisfactory briquettes could be made from the finer grinds. With the coarser grinds produced by the Raymond impact mill and the Raymond hammer mill with grates of $\frac{1}{8}$ -in. or smaller, briquettes could be made without precompression. Quite as hard briquettes with no greater circulating load of fines

were made with the coarser grind of calcine as had been possible with the finer grind plus precompression.

Since the production of good briquettes is essential, it was recommended that the grinding be arranged to produce a material that will briquette as readily as possible.

Mixing

The vane type of mixer produced a batch that was quite uniform in appearance. In an effort to improve this mixing in the early stages of the work, the material from the ribbon mixer was run through the Raymond hammer mill with a $\frac{1}{16}$ -in. grate. It was hoped that an improvement in the intimacy of mixing would result in improved yields. The experiments, however, showed no change. A possible explanation of this result appeared later when it was found that the yield was relatively independent of particle size below a given maximum, hence extraordinarily intimate mixing would be unlikely to improve the yield.

Catalysts

Several catalysts, including fluorspar, had been tried in the laboratory work preceding the pilot-plant operations. The use of fluorspar as a catalyst in the production of magnesium has been referred to in the literature and various early patents. The fluorspar is added either to the calcine or to the raw rock prior to calcination.

Little effect had been observed in the laboratory tests with 1 per cent fluorspar or with a number of other addition compounds. In the pilot plant the effect was also somewhat elusive. In early tests with the addition of 2 per cent fluorspar to the mix no effect was observed. Subsequent tests with more finely ground catalyst showed the first definite beneficial effects on yields with Gould dolomite. Further tests with some other dolomites and the same finely ground fluorspar showed small effects.

The effect of fluorspar on reactivity of Gould dolomite in the 10-in. retort is shown in Table 12. The sample of fluorspar contained about 88 per cent CaF_2 , was ground to better than 90 per cent minus 200-mesh and was used at the concentration of 2 per cent of the weight of calcine and ferrosilicon. The silicon efficiency increased 6 to 10 per cent.

This result of a 5 to 10 per cent increase in yield with the addition of a 2 per cent fluorspar was confirmed by further tests in the 8-in. retorts. These runs are summarized in Table 12 also, where two test runs at each

TABLE 12.—*Effect of Fluorspar*
Gould dolomite.

Mol ratio 1.25:1.

Ferrosilicon 79.2 per cent Si; minus 65-mesh.

Mix	Silicon Efficiencies		
	6 Hr.	7½ Hr.	9 Hr.
10-inch retorts. Temperature, 1170° to 1175°C.			
No fluorspar.....	74	81	82
2 per cent fluorspar.....	83 (86) ^a		88
8-inch retorts. Temperature, 1160° to 1165°C.			
2 per cent fluorspar.....	70, 77	89, 81	88, 88
No fluorspar.....	64.5	76.5	78.6

^a 6½-hr. run.

time may be compared with the averages of about five runs under identical conditions without fluorspar. It appears that fluorspar causes a distinct increase in yield when finely ground before addition to the mix, although discrepancies occurred occasionally in the use of other dolomites.

The final series of tests sought to determine the optimum concentration of fluorspar in the mix. The fluorspar used was from the same shipment as that employed in the experiments just described. A chemical and screen analysis of a sample taken after grinding showed the results listed in Table 13.

The additions of fluorspar were varied from 2 to 8 per cent of the weight of calcine plus ferrosilicon. The results include runs at mol ratios 1.15:1 and 1.25:1. While the

nearer the lower percentages of fluorspar as the time is increased. In other words, a smaller amount of catalyst at a longer heating time is more effective than the reverse.

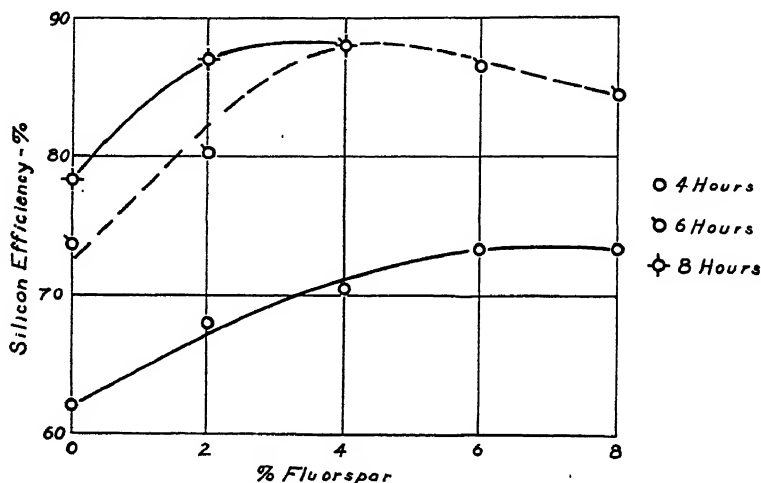


FIG. 19.—EFFECT OF FLUORSPAR.

series is rather incomplete, especially at the higher contents of fluorspar, the data appearing in Table 14 indicate that in the first case the distinct increase in yields

Thus, the maximum in the 8-hr. curve is nearly reached with 2 per cent fluorspar while the same maximum value is reached with the 6-hr. runs at about 4 per cent.

TABLE 13.—Chemical and Screen Analyses

Chemical Analysis		Screen Analysis	
Component	Per Cent	Mesh	Per Cent
CaF ₂	88.5	+ 30	1.0
SiO ₂	0.4	+100	2.5
R ₂ O ₃	3.6	+200	2.5
CaCO ₃	2.2	-200	94.0
BaSO ₄	0.5		
Moisture.....	0.1		
	95.3		

with the addition of 2 per cent fluorspar is confirmed, and in the second that silicon efficiencies do not increase beyond the 4 per cent addition of catalyst in the 6-hr. and 8-hr. tests. The increase on adding 2 per cent is apparently as great with the lower excess of dolomite as with the higher. The results of the runs at 1.25:1 mol ratio are plotted in Fig. 19. The curves indicate a maximum at each time, which is

TABLE 14.—Effects of Concentration of Fluorspar

Gould Dolomite. Temperature, 1160°–1165°C. Ferrosilicon, 78.5 per cent Si, minus 65-mesh.

CaF ₂ in Mix, Per Cent	Mol Ratio	Silicon Efficiencies		
		4 Hr.	6 Hr.	8 Hr.
0	1.15:1	62.5	74.0	76.0
2	1.15:1	72.7	80.5	83.5
0	1.25:1	62.1	75.3	78.3
2	1.25:1	68.0	80.3	87.0
4	1.25:1	70.5	88.0	88.0
6	1.25:1	75.5*	86.5	
8	1.25:1	75*	83.5	

* Single run.

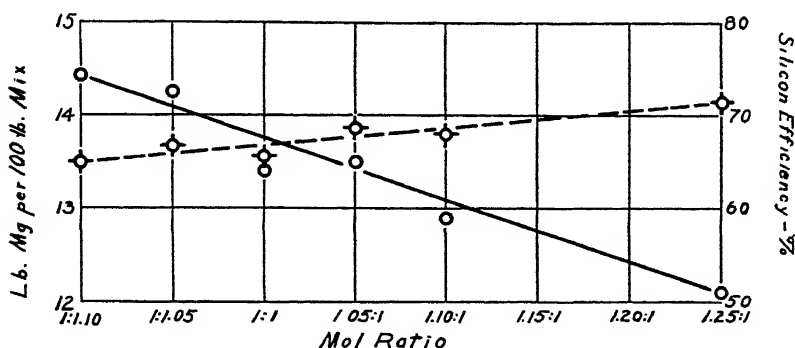
No catalysts other than fluorspar were tried in the pilot plant, since previous work had failed to disclose a superior catalyst.

Mol-ratio Relations

The mol ratio of the reactants was considered an important factor from the first.

From mass-law considerations, the constituent present in the smaller proportion will react to a larger extent. The chemical reactivity of the respective constituents

tests indicated. While there are some inversions in the 4-hr. and 6-hr. results, the trends are predominantly toward a small reduction in silicon efficiency with decreas-



Reaction Temperature 1160-5 °C
 Gould Dolomite
 Ferrosilicon 75.5 % Si, -65 Mesh
 Six Hour Runs—○ Lbs. Mg per 100 lbs. Mix
 ◊ Silicon Efficiency

FIG. 20.—INFLUENCE OF MOL RATIO.
 (Work done since Aug. 1, 1942.)

will also be an important consideration in the choice of mol ratio, since this will be a major factor in the efficiency of the reaction. In commercial operation, of course, economic considerations are paramount, and the ratio giving lowest over-all cost will be chosen.

During the course of the pilot-plant experiments, the mol ratio of the reactants was varied from 10 per cent excess ferrosilicon to 25 per cent excess dolomite. It was soon found, as had been the case in small-scale experiments, that a mixture with 25 per cent excess dolomite gave a considerably higher and a more reproducible silicon efficiency than a 1:1 ratio. Accordingly, the larger proportion of the earlier runs were made with 25 per cent excess dolomite in the mix, with frequent tests at lower mol ratios.

The effect of mol ratio on the silicon efficiencies is shown in Table 15, which is made up of the averages of the numbers of

ing excess of calcine. The decrease is never over about 5 per cent from 25 to 5 per cent excess calcine.

TABLE 15.—Effect of Mol Ratio on Yields Gould dolomite.
 Temperature, 1160° to 1165°C.

Si in FeSi, Per Cent	Mol Ratio	Silicon Efficiency, Per Cent			Runs at Each Time
		4 Hr.	6 Hr.	8 Hr.	
83.0	1.25:1	61.6	73.4	76.9	8 to 10
	1.15:1	61.3	71.3	76.1	6 to 14
	1.10:1	62.7	72.7	75.3	3
	1.05:1	57.3	67.6	72.3	3
79.2	1.25:1	64.5	76.5	78.6	4 to 5
	1.15:1	64.0	73.0	76.4	8 to 9
78.5	1.25:1	63.7	75.3	78.3	9 to 15
	1.15:1	62.5	74.0	76.0	2 to 7
75.4 ^a	1.25:1	61.0	67.3	77.7	2 to 6
	1.15:1	65.5	67.3	77.5	2 to 3
	1.10:1	61.1	72.7	76.3	9 to 15
	1.05:1	59	69	72	Single runs

^a Work done since Aug. 1, 1942.

The mol ratio of ferrosilicon in the charge was increased to 10 per cent excess

in a set of runs where the tests were made at 6 hr. reaction time. The results are plotted in Fig. 20, where the silicon efficiencies and pounds or units of metal per 100 units of briquettes are plotted on the respective ordinates and the mol ratio is shown as the abscissa. The curve of silicon efficiency versus mol ratio shows a small positive slope. On the other hand, the weight of metal produced per given amount of charge increases by a much larger proportion. The curve appears to be linear in this case also.

Theoretical calculations giving the limitations of results attainable by varying the mol ratio widely on each side of the equimolecular proportion are shown in Table 16. The second column gives the weight of metallic magnesium that would be produced at 100 per cent reaction efficiency. This value goes through a maximum at the equimolecular ratio and falls slowly on either side.

Columns 3 to 5 show the silicon efficiencies necessary to produce 12.0, 13.6 and 15.0 units of magnesium from 100 units weight of mix at the various mol ratios.

TABLE 16.—*Calculated Efficiencies Required to Produce a Given Yield of Metal*
Ferrosilicon, 75.5 per cent.
Dolomite, 24.3 per cent Mg in calcine.

Mol Ratio, Calcine: Si	Mg per 100 Lb. Mix, Lb.	Per Cent Silicon Efficiency Required to Produce		
		12.0 Lb. per 100 Mix	13.6 Lb. per 100 Mix	15.0 Lb. per 100 Mix
1.25:1	16.9	71.0	80.5	88.8
1.10:1	18.9	63.5	71.7	79.5
1.00:1	20.5	58.5	66.5	73.2
1:1.10	20.2	54.1	61.3	67.6
1:1.25	19.7	48.7	55.2	60.8

In plant practice, the relative cost of ferrosilicon compared with general operating costs will dictate the optimum ratio to be employed. If operating costs are high, every attempt will be made to produce a large amount of metal in a short

time. In other words, excess silicon might be employed and the retort operated on short cycles.

Briquetting and Briquette Size and Shape

The early tests were made with pellets of $\frac{3}{4}$ -in. diameter by about $\frac{1}{4}$ in. thick, produced by a rotary tablet machine as described under Apparatus. This machine was soon found unsuitable for producing briquettes in large quantities and the larger, more rugged Southwark press was used. These pellets were first crushed and the fraction $-\frac{1}{2} + \frac{1}{4}$ in. was used in some early reduction experiments. Uncrushed briquettes (2-in. dia. by $\frac{3}{8}$ to $\frac{5}{8}$ in.) gave improved yields. These larger briquettes were then used in all subsequent experiments until Komarek "ovoids" became available.

The apparent density of the loose powdered charge was about 0.6. The briquette density lay between 2 and 2.2. The bulk density of Southwark pills was about 0.97 (61 lb. per cu. ft.). Similar Komarek ovoids were denser; i.e., 1.09 (68 lb. per cu. ft.).

The calcine-ferrosilicon mixture is relatively abrasive and the wear on any briquetting or pelleting machine used is rather rapid. To decrease this wear and assist in the flow of the particles to form a hard, dense pellet, it was thought that "lubricants" might be useful.

Any added material must conform to the requirement that it does not decrease the yield by reacting with the silicon or magnesium vapor at any part of the cycle. Water-base materials and most compounds containing oxygen, such as carbohydrates, produce water, carbon monoxide, etc., on thermal decomposition, which would be reduced by the magnesium vapor, with consequent loss in yield. If, on the other hand, the volatile matter is removed by preheating, a porous briquette is produced, which reduces the retort capacity.

With these limitations in mind, only two lubricants were tried; viz., graphite and talc. Various grades of graphite in various mesh sizes were used but no beneficial effect could be observed in any of the trials. The graphite was added to the mixer before mixing and amounted to 1 per cent of the mixture. Talc was similarly tried but showed no noticeable beneficial effects. It was further found in laboratory experiments that the addition of graphite decreased the yield of magnesium appreciably, therefore its use was abandoned.

A comparison of the efficiency of the crushed briquettes versus the whole briquette in the 8-in. retort is shown in Table 17. With the exception noted, the values are arithmetical averages of a number of runs. This shows that the whole briquettes gave a distinctly better yield at all times, and especially at the shorter time, suggesting a slower heat penetration with small briquettes. A much more important factor is the occurrence of large quantities of dust and small particles in the charge. Undoubtedly the presence of the latter in uncontrolled amounts was responsible to some extent for lack of reproducibility frequently encountered in these experiments.

TABLE 17.—*Comparison of Whole Briquettes with Fragments*

Portage du Fort Dolomite.

Temperature, 1120° to 1125°C.

Ferrosilicon, 85.6 per cent Si; minus 200-mesh.

Mol Ratio, 1.25:1.

Briquette	Silicon Efficiencies		
	4 Hr.	6 Hr.	8 Hr.
Fragments, $\frac{1}{2}$ + $\frac{1}{4}$ in.	49.5 ^a	64.7	69.4
Whole briquettes, 2-in. by $\frac{1}{2}$ in.	57.9	70.2	74.0

^a Average of two runs.

A small sample of Komarek-Greaves briquettes made at Chicago in the form

of flattened ellipsoids 1 by $\frac{3}{4}$ by $\frac{7}{8}$ in., approximately, was tested with the 8-in. retort in the pilot plant and compared with Southwark pills. The results of this test are summarized in Table 18. Little difference in yield is shown, except at the shorter times when the Komarek ovoids gave lower recovery.

TABLE 18.—*Comparison of Southwark with Komarek-Greaves Briquettes*

Portage du Fort Dolomite.

Temperature 1145° to 1150°C.

Ferrosilicon, 76.5 per cent Si.

Mol Ratio, 1.25:1.

Briquette Variety	Silicon Efficiencies			Remarks
	4 Hr.	6 Hr.	8 Hr.	
Komarek-Greaves	53	74	81	Single runs
Southwark.....	59.2	74.3	80.0	
				Averages

From a theoretical point of view, the results described in the foregoing paragraphs may be explained as follows. In a single briquette supplied with adequate heat by radiation, the rate of reaction will increase with decreasing size of the briquette, owing to the shortened vapor-diffusion path. When the reacting mixture is a number or mass of individual briquettes, most of these must receive their heat largely by radiation through the interstices of the mass. These interstices are larger when the individual briquette is large, providing a more open radiation path. It will then be readily seen that there should be an optimum size of briquette for a reacting mass of given dimensions.

The broken $\frac{1}{2}$ -in. pieces were too small to permit rapid inflow of heat to the mass, although the vapor readily escapes from the individual briquette. In agreement with this, $\frac{1}{2}$ -in. fragments were used successfully in small-scale experiments, where the dimensions of the reacting charge were much smaller. A reasonable balance would appear to have been struck between the two effects in the case of the Southwark

tablets. The lack of essential difference between the yields with the Southwark and Komarek-Greaves briquettes would indicate that there is a fairly wide range of sizes where the two factors are sufficiently well balanced for practical purposes.

These considerations, of course, forbid the use of unbriquetted powder or any similar mass of briquettes plus powder with small interstices. It is thus important to use briquettes sufficiently hard to resist attrition by handling, etc. The validity of this requirement was demonstrated frequently in the pilot-plant work when soft briquettes were used which had been partly reduced to powder. The yields were always distinctly lower in these cases. The effect was more pronounced in the tests in the 10-in. retort. Fortunately the Southwark pellets were very strong and showed little tendency to disintegrate.

Preheating

The charge was preheated during most of the experiments. An early group of experiments carried out to find the upper limit of temperature of preheating are shown in Table 19.

TABLE 19.—*Effect of Preheating*

Portage du Fort Dolomite.

Mol Ratio, 1.25:1

Temperature, 1145° to 1150°C.

Time, 6 hours. Preheat time, 4 hours (2½ hours at stated temperature).

Preheat Temperature, Deg. C.	Pressure, Mm. Hg after				Silicon Efficiency, Per Cent	Grade of Deposit
	15 Min.	30 Min.	60 Min.	Final		
None...	8.5	0.7	0.30	0.12	76	B
820....	0.4	0.16	0.10	0.05	76	A
915....	0.2	0.08	0.05	0.03	74	A
955....	0.3	0.2	0.12	0.08	72	A

No improvement in yield was achieved by preheating. The quality of the metal was notably improved, however. The sensible heat of the charge, which is provided by preheating to 750°C., is approximately 14.6 per cent of the total

theoretical requirements. In cold charging, this energy is readily supplied in the retort, owing to the favorable temperature gradient (assuming the furnace can supply the extra heat). From thermal considerations, therefore, an improvement of yield is unlikely to follow preheating. A number of experiments comparing preheating with immediate closing of the retort were carried out. Special precautions were taken in the grinding, briquetting, etc., of the calcine in order to minimize moisture pickup. In general, little difference in yield could be observed and deposits of good quality were obtained.

The practice of preheating in the retort at the operating temperature with the head off definitely lowered the yields—the longer the time, the lower the yield. Table 20 shows this clearly.

TABLE 20.—*Effect of Time of "Burn-off"*
Calcine from Dominion Magnesium Plant, Haley, Ontario.

Temperature, 1160° to 1165°C.

Mol ratio, 1.1:1.

Time of Preheat or "Burn-off," Min.	Silicon Efficiency, Per Cent	
	K. G. Briquettes	Southwark Briquettes
10	65	70
20	64	
30	62	67

* Work done after Aug. 1, 1942.

Under these conditions, much of the water is decomposed by the reducing agent and is evolved as hydrogen. To some extent, this hydrogen protects the silicon in the charge from atmospheric oxidation. The extent to which this takes place depends upon the geometry of the reacting mass. Different results would be obtained in retorts of different size. As with many other factors, plant practice must be a compromise, taking into account the vacuum practice and the ability of the briquettes to withstand handling. The ideal method is to avoid the pickup of moisture

by careful design of grinding, mixing and briquetting apparatus. The calcine, after all, has been outgassed in the kiln. With low moisture content, the retort may be closed immediately after charging.

CONCLUSIONS

On the basis of the work described, the following general conclusions were drawn:

1. Calcined dolomite and ferrosilicon in briquetted form will react in 8 to 10-in. i. d. heat-resisting steel retorts in vacuo at temperatures of 1150° to 1160°C., giving 70 to 80 per cent reaction of the silicon. A simple closed-end tube disposed horizontally forms a convenient system, which can readily be loaded and unloaded. The pilot-plant work indicated that full-scale operation could be achieved by lengthening the pilot-plant retort and placing a number of retorts in convenient furnaces. No fundamental change in practice would be involved by such a step.

2. Metallic magnesium is deposited in a simple tubular condenser inserted in the cold end of the retort. A massive deposit of crystals is secured by correct condenser design and temperature. Alkali metals must be separated effectively from the magnesium. The crown of magnesium is pressed from the condenser and the latter is returned to the retort. Crowns may be melted to ingot with not more than 3.5 per cent loss. The magnesium is exceedingly pure, Mg content being greater than 99.98 per cent.

3. The dolomite should be largely $\text{CaCO}_3\text{MgCO}_3$. Since high-purity stones are of widespread occurrence, there would appear to be no need for considering a dolomite with a $\text{CaCO}_3\text{MgCO}_3$ content lower than 97 per cent. Alkali metals if present should exist only in small concentrations.

4. The 75 per cent ferrosilicon grade appears to be the most economical grade to employ under existing market conditions.

5. At operating temperatures of 1150° to

1160°C. in a direct gas-fired furnace, a retort of dimensions i. d. 8 in., wall thickness $\frac{7}{8}$ in. and composition 35 Ni, 15 Cr steel indicated a life of at least 6 months. (Actually plant retorts of this size and composition have given 11 months service.)

6. Heat-resisting steels may be cast into retorts that may be made vacuum-tight. Pressures of the order of 0.1 mm. Hg are required to produce good deposits. Pressures below 0.5 mm. do not increase yields, but metal deposits are improved. Pressures as low as 0.002 mm. Hg were tried without improvement in yield.

7. With the high-purity dolomites employed, calcination temperature is not a vital factor, over a limited range at least. This conclusion applies to the reactivity of the charge itself. Calcination affects briquetting and therefore the process as a whole.

8. Particle size of calcine and ferrosilicon does not appear to be critical provided a reasonably fine subdivision is achieved. Minus 65 mesh for ferrosilicon and 30 per cent -30+100 and 30 per cent minus 200 mesh for calcine are suitable. In general, grinding should be adjusted to facilitate briquetting.

9. Strong, dust-free briquettes of density in excess of 2.0 are most desirable. Briquetting experiments described in this paper involved only two types of piston press. The following observations were made:

- a. Crystalline dolomite produced calcines more readily briquettable than the microcrystalline variety.

- b. A wide range of particle sizes assists briquetting.

- c. Precompression assists briquetting and is, in fact, essential with some calcines.

- d. Lubricants such as graphite did not improve briquetting when added in the small amounts permissible.

10. Retort output and silicon efficiency are to a certain extent inversely proportional, as shown in the following table.

Assume 8-in. retorts holding 100 lb. of charge.

Cycle Time, Hr.	Silicon Efficiency, Per Cent	24-hr. Output, Lb.	Lb. per 24 Hr. per Sq. Ft. of Hot Retort Surface
4	65	66.0	7.8
6	77	52.2	6.2
8	80	40.7	4.8

The plant operator, striving always to cut costs, will choose an operating cycle to suit his particular conditions.

11. The externally heated retort, if fuel fired, permits the production of magnesium by the use of approximately one half the electrical energy of the established electrolytic process, and this energy is alternating current—not direct current. This is shown in the table below, where it is assumed that one short ton of 75 per cent ferrosilicon requires 8000 kw-hours.

Silicon Efficiency, Per Cent	75 Per Cent Si Consumed per Lb. Mg Produced, Lb.	Basic Power, Kw-hr. per Lb.
65	1.21	4.84
70	1.12	4.48
75	1.05	4.20
80	0.98	3.92

12. When dolomite is present in excess, silicon efficiencies are highest but metal output per retort may be lower. The choice of ideal ratio again depends upon many

factors, and cannot be made in the pilot plant.

13. With correct condensing conditions, the hot magnesium condensate may be removed in air without special precautions such as inert gases or shock chambers.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Dominion Magnesium Limited for permission to publish these results. Acknowledgment is also made to E. A. Brown, D. A. Tetu and many other loyal assistants at the National Research Laboratories, who spent numerous days and nights conducting these experiments. The work was greatly facilitated by the active cooperation of the Mines Branch Laboratories, Ottawa, where all preparation of the raw material took place.

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Vacuum Engineering as Related to the Dolomite Ferrosilicon Process

By W. B. HUMES*

(New York Meeting, February 1944)

THE use of high vacuum on a large industrial scale in the ferrosilicon process for the production of magnesium marks the coming of age of an important new metallurgical technique. The economical production of reactive metals, such as magnesium, which combine with all the well-known furnace atmospheres, has until recently been successfully carried out only by electrolytic methods. It is now apparent that, through the use of high vacuum, the distillation or sublimation of many metals can be done industrially at much lower temperatures, and hence in much simpler equipment, than heretofore has been thought possible.

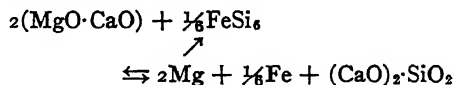
At the beginning of the present emergency, when the ferrosilicon process of producing magnesium was brought to the fore, little was generally known about vacuum engineering, practices, and techniques. In a comparatively short time, the available equipment has been adapted, new equipment designed and built, and a fund of know-how evolved to make possible the production of thousands of pounds of magnesium per day at pressures less than 1/10,000 of an atmosphere.

Pilot-plant operations have been consistently maintained at pressures even as low as one micron (0.001 mm.). These low pressures, which previously were regarded as prohibitively costly or impossible to

attain, have been demonstrated as economically feasible on an industrial scale.

NECESSITY FOR VACUUM

The main function of vacuum in the ferrosilicon process, and hence in most vacuum smelting processes, is to lower the temperature at which the metal may be distilled or sublimed from the reduction mixture. A secondary function is to protect the distilled metal from attack by the furnace atmosphere and to permit the formation of a dense condensate. In the ferrosilicon process, magnesium is formed by the reaction between dolomite and ferrosilicon:



The metal is distilled from the pelleted charge at a free air pressure of about 0.100 mm. of mercury (100 microns). This low pressure is not needed for the reaction, but rather serves to protect the metal vapor from the oxygen or nitrogen of the atmosphere and permits the formation of a condensate free of pyrophoric material. The reaction proceeds at air pressures as high as several millimeters of mercury, and evidence has been offered to show that the actual equilibrium pressure of magnesium at operating temperatures of 2150°F. is somewhat higher. Experimentation indicates that the yield begins to decrease at pressures above 500 microns.

While no real operating data are yet available on the relationship between

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vacuum and yield and between vacuum and quality, the plants operating at the higher vacuums have shown the lowest melting losses. It must be noted, however, that melting loss is not entirely a function of metal quality, but also may depend somewhat on the method of operation.

The fact that the yield seems to fall at air pressures in the vicinity of 500 microns does not necessarily mean that the reaction is impeded by the high pressure. It may be that the magnesium vapor oxidizes upon formation and thus remains in the charge. Sight-glass observations confirm the fact that actual burning of deposited magnesium occurs at pressures as low as 1000 microns (1.0 mm.).

The effect of pressure upon the quality of the condensate has been clearly demonstrated. At pressures above 500 microns, a deposit containing relatively large quantities of oxide, nitride, and pyrophoric dust is formed. If sodium and potassium are present, as in most dolomites, these metals usually burst into flame and ignite the pyrophoric magnesium during the discharging of the retort. At lower pressures, a dense metallic crown is formed, low in impurities and difficult to ignite.

Magnesium begins to be evolved, depending somewhat on local conditions, about one hour from the time the furnaces are charged, assuming a retort temperature in the vicinity of 2150°F. It is essential, therefore, that the pressure be reduced to working range before that time. If a prolonged evacuation cycle occurs, the crown of metal condensate is surrounded by a loose, granular deposit, which makes removal from the condenser difficult and greatly increases subsequent melting loss.

The evacuation of the retorts alone does not require appreciable pumping capacity, four retorts being evacuated in a few minutes by a pump working at a rate of 100 cu. ft. per min. However, the briquettes contain considerable quantities of absorbed and chemically combined gas and water

vapor, and hence are the chief cause of the pumping problem. Some of the combined gas and water is liberated only when the charge becomes heated, and thus high pumping capacity is needed beyond the period of initial evacuation.

METHOD OF PUMPING

It has been shown at the ferrosilicon plants that the economical operating temperature for alloy retorts is in the vicinity of 2150°F., and that an 8-hr. cycle is about optimum. Under these conditions, it is desirable that an operating pressure of 100 microns or lower be maintained, and that that pressure be reached within one hour from the time of charging. A high-speed vacuum system, in which pumping is continuous even when the operating pressure is reached, is used because of leaks and outgassing of the various metal parts and the charge. It is readily discernible that the vacuum pumps perform two functions:

1. They provide for the initial evacuation in which large volumes of gas are produced at relatively high pressures.
2. They supply pumping speed at low pressures for the remainder of the cycle.

At the outset of the program, it was tentatively agreed that four retorts would be manifolded and operated as a unit. Each unit was to have one mechanical pump of 100 cu. ft. per mm. capacity, for maintaining vacuum, and each group of four or five units might have one or more additional pumps for evacuation during the roughing cycle.

The following possibilities were available for the production of the required pressures: (1) rotary oil-sealed mechanical vacuum pumps, (2) multistage steam jet ejectors, (3) diffusion pumps in combination with suitable backing pumps.

The mechanical pumps were available in several useful sizes ranging from 25 to 600 cu. ft. per min. capacity. Steam jet ejectors had not had widespread applica-

tions at pressures in the micron range, and, because of their large size, complicated valving and piping systems would have been necessary for use in the ferrosilicon process, since most plants have many small

pump. With these pumps available, new vacuum systems have been developed which have enabled much faster evacuation cycles and lower ultimate operating pressures.

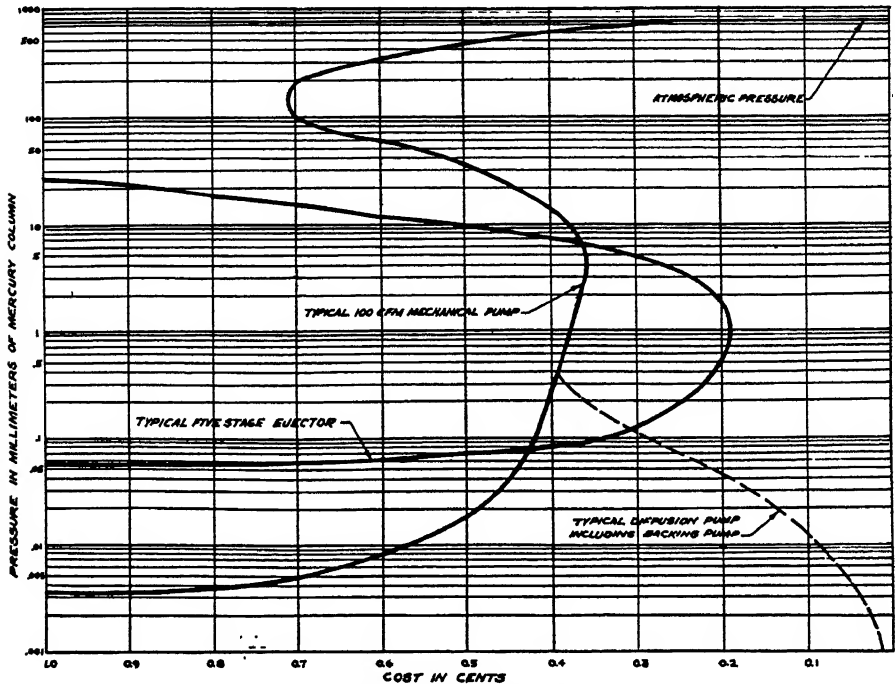


FIG. 1.—PUMPING COSTS FOR SEVERAL TYPES OF PUMPS, BASED ON 24-HOUR OPERATION.
 Cents per 1000 cu. ft. at various pressures.
 Power @ \$0.008 per kw-hr.
 Water @ \$0.02 per 1000 gal.
 Steam @ \$0.30 per 1000 lb.
 Amortization @ 20 per cent.

retorts. No large diffusion pumps were available that combined high speed in the range 1 to 500 microns with the ability to operate against high fore pressures.

During the construction of the magnesium plants, industrial diffusion pumps using both oil and mercury vapor were developed for the process, and since have been adopted by several of the operators. These pumps, which have extremely large gas-handling capacities at pressures below 1000 microns (1 mm.), must be used in combination with a suitable backing pump, such as a rotary mechanical

Steam jet ejectors have been employed successfully in one plant that used a small number of very large retorts. A long evacuation cycle plus the large unit vacuum system makes steam jet ejectors particularly applicable in this installation.

Experience in operating has shown that probably there is a place for all three of the types of pumps so far mentioned; that is, the steam ejector is valuable for handling extremely large quantities of gas at moderate pressures while the mechanical pump is useful through the entire range of pressures involved in this process. Diffu-

sion pumps have already demonstrated their practicability in the lower pressure ranges. It is probable that for future operations various combinations of these

nomical between 0.1 and 10 mm. pressure, and therefore should be useful where large-scale installations make possible an efficient operation.

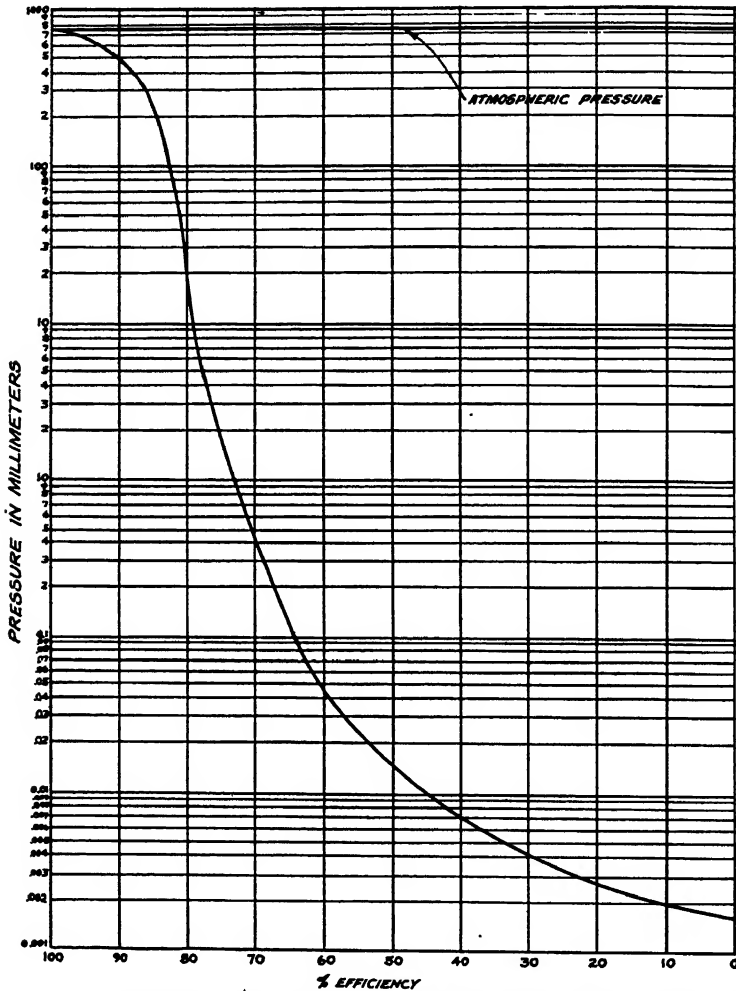


FIG. 2.—TYPICAL VOLUMETRIC EFFICIENCY CURVE FOR MECHANICAL VACUUM PUMP OF 100 CUBIC FEET PER MINUTE CAPACITY.

three pumping means will be evolved to provide maximum efficiency.

Fig. 1 shows the relationship between the pumping costs of these types of pumps based on typical data supplied by leading manufacturers. It is apparent from this graph that the steam jet ejector is eco-

Any interruption in the operation of a steam jet ejector, such as the clogging of a jet or a shutdown on the steam supply, would cause an immediate rise in pressure, with the possibility of forcing steam or water into the retorts. This has caused many operators to reject them. When

suitable protective devices are available, it is possible that wider use will be made of ejectors, particularly during the roughing cycle.

The speed of the mechanical pump, as shown by the volumetric efficiency curve in Fig. 2, is rapidly decreasing in the vicinity of the working pressure. Actually, the mechanical pump efficiency may be much less than the curve would indicate unless the pump is supplied with a continuous stream of purified and dried oil. Throughout the early stages of the process, water vapor is liberated from the charge. If this is allowed to contaminate the pump oil, serious losses in pumping speed are apparent, even with moisture values of less than 0.05 per cent. This, then, imposes upon the mechanical pump an additional operating cost; that is, a continuous supply of pure oil. Since each 100-cu. ft. mechanical pump requires in the vicinity of 8 gal. of oil per hour, a rather elaborate oil-purification system must be provided. It is apparent that for operating pressures in the vicinity of 100 microns or lower, the diffusion pump is the most economical means of vacuum pumping. Actually, the performance of diffusion pumps when used in the ferrosilicon process is somewhat better than is indicated by the curves in Fig. 1, because the process gas during much of the cycle is composed largely of hydrogen. Since the ability of the diffusion pumps to handle gas varies inversely with square root of the molecular weight of the gas, their relative efficiency is improved by the presence of hydrogen. The mechanical pump, on the other hand, depends for operation only upon the displacement of the pump itself rather than upon the rate of diffusion of the gas molecules.

The maintenance problem is covered in Table 1. This applies only to the various pumps as utilized in the ferrosilicon process, where they are subjected to dust and water vapor. When any of the pumps are used on systems handling only clean, dry air,

maintenance problems are substantially negligible.

The chief advantage of the mechanical pump is that, while having pumping speed in both the high and low pressure ranges, it is economical in relatively small units. Thus, it is possible to avoid complicated valving and piping arrangements and still obtain reasonable vacuum conditions.

The pumping speed of properly designed multijet diffusion pumps is independent of fore pressure conditions over a wide range; that is, 0 to 2 mm. or more. In an

TABLE 1.—*Maintenance of Pumps in Ferrosilicon Process*

Pumps	Effect of Dust	Effect of Water Vapor	Ease of Cleaning	Wear	Frequency of Pumping Fluid Change
Mechanical.	Poor	Poor	Poor	Fair	Poor
Diffusion...	Fair	Good	Poor	Good	Good
Ejectors....	Fair	Good	Fair	Good	Excellent

installation using a diffusion pump in combination with mechanical pumps, the latter may be permitted to absorb a considerable amount of water before the pumping fluid is sufficiently contaminated to cause an elevation in the fore pressure of sufficient magnitude to interfere with the operation of the diffusion pumps. The actual power cost of the various systems is large in comparison with maintenance and depreciation and, together with considerations of operating efficiency, should be the deciding factor in any installation.

OPERATING CYCLE AND TYPICAL INSTALLATIONS

Most of the plants using the ferrosilicon process have retorts about 8 ft. long and 10 in. in inside diameter, making a volume, including the condenser space, of about 6 cu. ft. Four of these retorts are connected to a manifold and operated as a unit. The time necessary to evacuate this volume is given by the equation

$$T = \frac{V}{D} K$$

where T is the evacuation time, V the volume of the system, D the pump displacement in cubic feet per minutes, and K a constant depending on the desired pressure. In the ferrosilicon systems

$$V = 24 \text{ cu. ft.}$$

$$K = 8 \text{ (for } 0.100 \text{ mm.)}$$

$$D = 100 \text{ cu. ft. per min.}$$

$$T = \frac{8 \times 24}{100} = 2 \text{ min. (approximate)}$$

Actually, this condition is realized only when there is no impedance in the pipe lines between the vacuum system and the pump, and no leakage or outgassing. In actual plant operations this has not been feasible, and in many places the pumps and retorts are placed on different levels, necessitating pipe lines approximately 50 ft. long. For calculating the pumping speeds of pipe systems, the general formula* for inlet speed, S_{inlet} is given by

$$\frac{1}{S_{\text{inlet}}} = \frac{1}{U} + \frac{1}{S_{\text{pump}}}$$

where U is given by

$$U = 510 \frac{D^4}{L} P - 14 \frac{D^3}{L} \frac{(1 + 620DP)}{(1 + 760DP)}$$

U is in cubic feet per minute, D is the pipe diameter in inches, L is the length in feet, and P is the average line pressure in millimeters of mercury.

The relation between inlet speed and pressure as determined from these equations for a 3-in. pipe 50 ft. long is given in Fig. 3, assuming a 100-cu. ft. per min. mechanical pump with a volumetric efficiency as indicated in Fig. 2. At 100 microns the piping is 58 per cent efficient, which is only a fair condition.

It is evident from these calculations

that, if pumps with high capacities in the lower range are used, either the pumps must be placed close to the retorts or the pipes must be considerably larger.

A typical installation using only mechanical pumps is shown in Fig. 4. In operation, one bank of four retorts is charged and then evacuated in approximately one hour, using the holding pump for that bank and the roughing pump or pumps for that furnace in parallel to get high capacity during the early part of the cycle. The roughing pumps are then valved off and the retort bank is left on one holding pump. The second bank of four retorts is then charged and the cycle repeated.

This type of installation offers several difficulties from an operating standpoint. A charging crew cannot simply move down the line of retorts, charging every bank in turn, but must load one bank of retorts in every furnace, and then repeat the charging operation four times. This feature wastes motion and time, and, coupled with the fact that the operator must cope with relatively complicated valving arrangement, makes the arrangement impractical.

At least one of the operators has preferred to eliminate the extra pumping speed of the evacuation cycle and use only the holding pumps. When this operation is used, the retort banks may be charged in order, and the operator has only simple valving operations. However, the pumping speed of one pump is not adequate and poor metal has resulted from this system.

A fairly simple and efficient operation has been evolved using mechanical pumps and diffusion pumps (Fig. 5). In this operation, the five retort banks of an entire furnace are charged in order and evacuated by the roughing pumps. At the end of the roughing cycle, the roughing valves are closed and the system is put on the diffusion pumps, which rapidly complete the evacuation and maintain working pressure throughout the cycle. The disadvantage of this system is the fact that the roughing

* M. Knudsen: *Ann. Phys.* (1908) 28, 75, 999.

pumps are utilized less than two hours out of every eight. It has been proposed that a master roughing line with a steam ejector be installed in conjunction with this system

Typical vacuum cycles for the various pumping systems are shown in Fig. 6. These are composite curves based on results in the many plants, and it must be

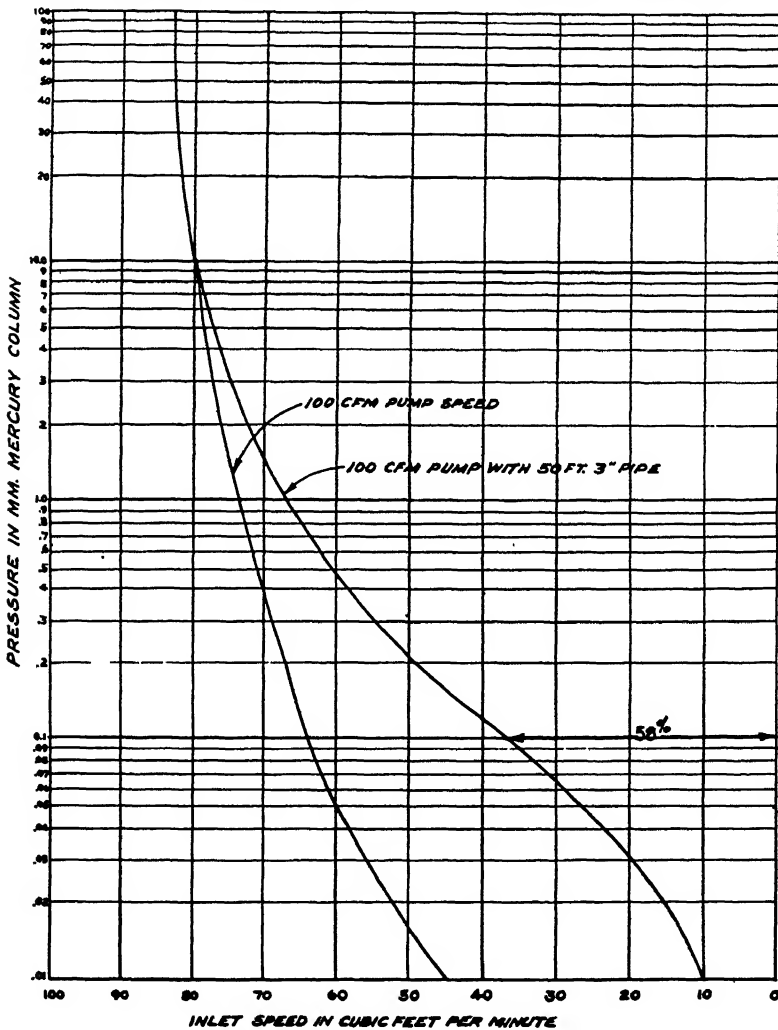


FIG. 3.—INLET SPEED OF PIPING SYSTEM, MECHANICAL PUMP OF 100 CUBIC FEET PER MINUTE CAPACITY.

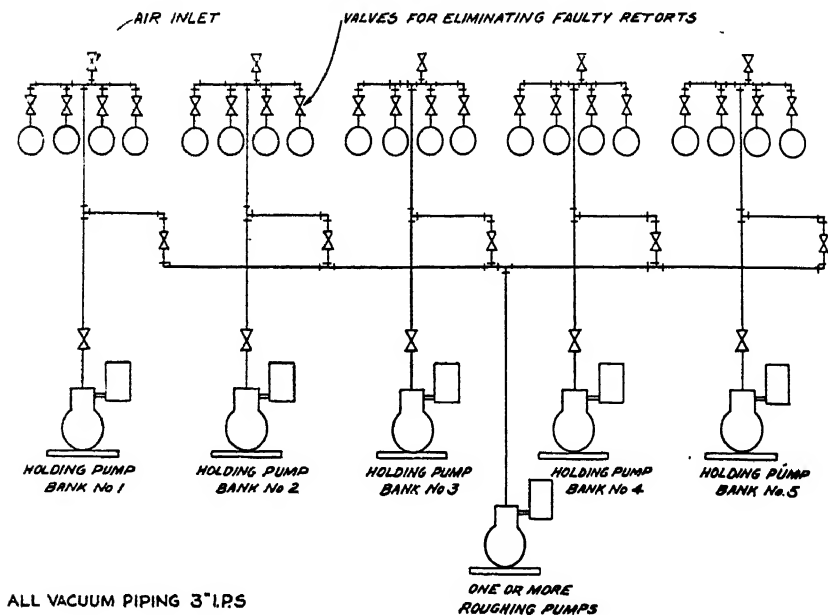
Cubic feet per minute for 50 feet of 3-inch pipe.

and the roughing pumps be eliminated. An ejector could be used for the evacuation in the range of low pipe impedance, and the diffusion pumps, placed close to the retort banks, would handle the pumping in the lower pressure range.

emphasized that better or worse performances may be obtained.

MEASUREMENT OF PRESSURE

Attendant on the problem of producing vacuum in the ferrosilicon process has been



OIL PURIFICATION SYSTEM NOT SHOWN.

FIG. 4.—TYPICAL MECHANICAL PUMP INSTALLATION, TWENTY-RETORT FURNACE.

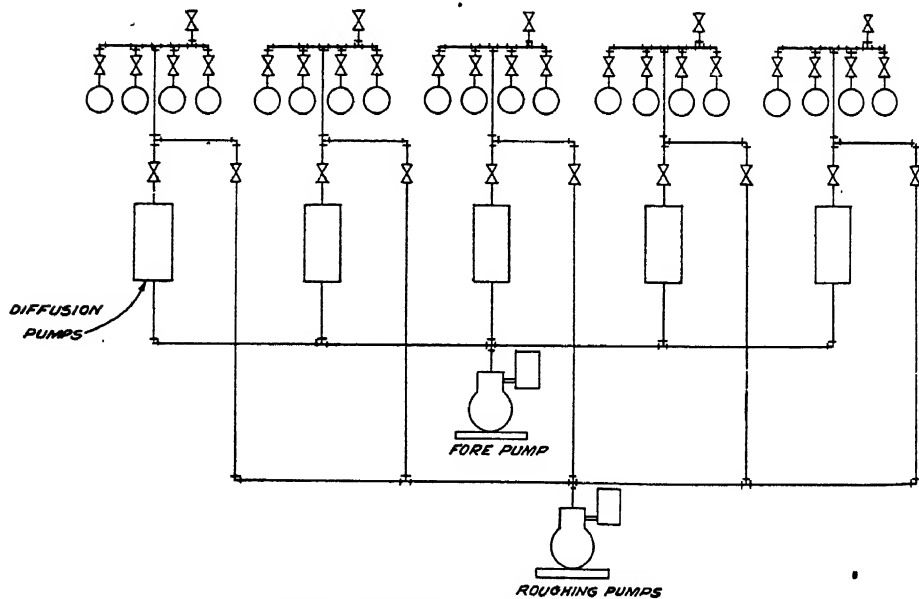


FIG. 5.—TYPICAL DIFFUSION PUMP INSTALLATION, TWENTY-RETORT FURNACE.

the problem of measuring it. To date only two pressure instruments have had widespread usage in magnesium plants—McLeod gauges of the tilt type and thermo-

trapped and compressed into a small capillary by the action of a rising column of mercury produced by tilting the gauge or by elevating the mercury reservoir.

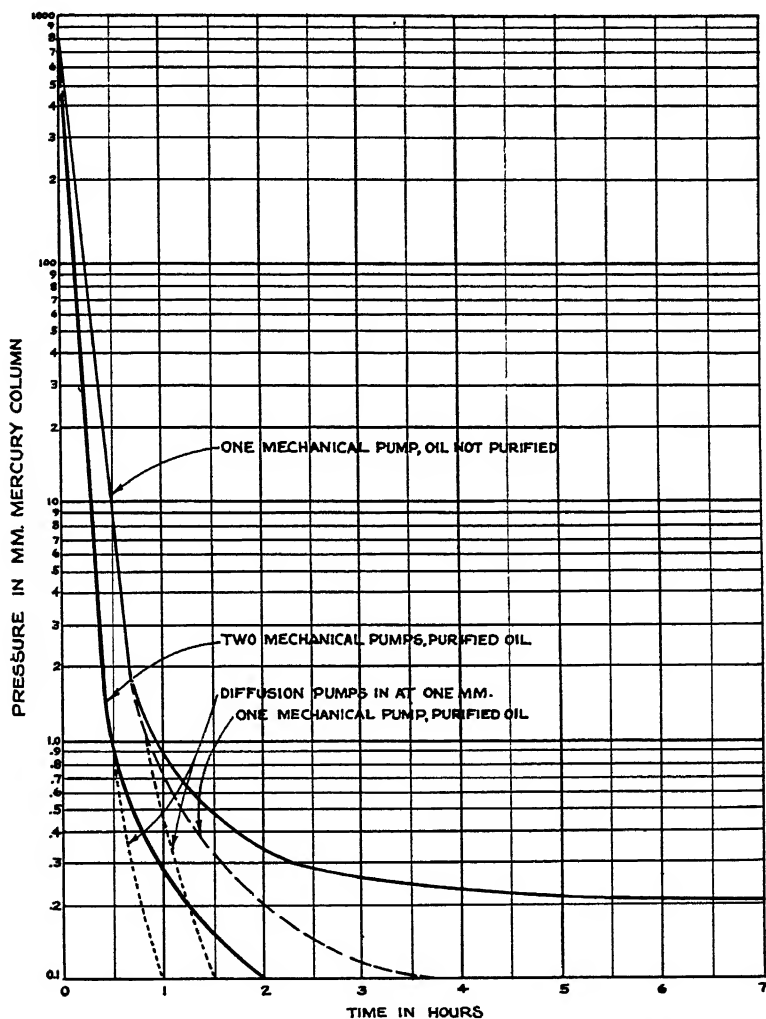


FIG. 6.—TYPICAL VACUUM CYCLES, FOUR-RETORT BANK FOR VARIOUS PUMPING SYSTEMS.

couple gauges. The former is an absolute instrument in which calibration is made from the dimensions of the gauge itself, whereas the thermocouple must be calibrated against a standard.

In the McLeod gauge, a known volume of gas at the pressure of the system is

The volume of the compressed gas as measured on a scale beside the capillary indicates the pressure. Inasmuch as the gas is compressed to obtain the pressure measurement, the McLeod does not accurately indicate the partial pressure of condensable vapors such as water, and the use of

a cold trap to remove condensable vapors is essential if accurate reading of free gas pressure is required.

In the thermocouple gauge, a known current is applied to the "heater" wire of the gauge giving a constant heat input. The temperature of that wire depends, as a result of the cooling effect, on both the number and type of gas molecules present to conduct heat away from it. Thus, the electromotive force generated by the thermocouple placed in contact with this "heater" wire can be translated in terms of pressure. The change in conductivity has the greatest effect between 1 and 1000 microns, which is the sensitive range of this gauge. The heater and thermocouple wires can be built into a metal envelope, and the gauge may be threaded directly into the piping. Continuous pressure records are obtained by means of a recording potentiometer, or an indicating device such as a special low-resistance microammeter may be used.

Care must be exercised in connecting vacuum gauges to the system as small leaks may obscure the readings, particularly if the gauge is placed at the end of a high-impedance pipe line. In general, it is best to have all gauges as near as possible to the point where pressure is to be determined.

VACUUM TECHNIQUES

Engineers have realized that, although the piping carries only a relatively small external pressure, it must be made extremely nonporous because of the tremendous expanded volume of a small leak at atmospheric pressure; for example, one cubic foot of air at atmospheric pressure occupies 7600 cu. ft. at 100 microns. Considerations of the leakage problem led to the use of welded piping and forged steel fittings. Threaded joints are treated with resin paints such as Gplytal. Rubber or composition gaskets are cleaned and wet with grease or oil before assembly. Lubri-

cated plug valves, up to 6-in. pipe size, have been used with success, although care must be exercised with regard to the lubrication and the condition of the valve-seat surfaces.

It has been found that new piping systems are best subjected to an initial pressure and "soap bubble" test, and that final tests can be made under vacuum. Where thermocouple gauges are used, vacuum leaks may be detected by spraying the suspected point with acetone or other volatile liquids or with hydrogen. As the vapor or hydrogen leak replaces the air leak, an apparent rise in pressure is noted on the gauge. Rate of leak tests may be used to determine tightness by valving off the system being tested and noting the rise in pressure as a function of time for a specific volume.

CONCLUSION

Through the ferrosilicon process, the large-scale application of pressures in the micron range has been demonstrated as commercially practical. The metallurgist has a new and proven atmosphere in which to carry out smelting and refining operations. While still in its infancy, vacuum technology has progressed from the laboratory to industry in a matter of a few years. Future large-scale applications of low pressures will depend to a large measure on the propagation of the data and know-how developed in the ferrosilicon process.

ACKNOWLEDGMENT

Much of the information presented in this article has been based on experience gained during the operation of a pilot plant at National Research Corporation under D. P. C. Plancor 708, which was sponsored by the Aluminum and Magnesium Branch of the War Production Board. Acknowledgment is also made of the valuable assistance of Dr. J. R. Downing, of National Research Corporation, in the preparation of this report.

Plant for Production of Magnesium by the Ferrosilicon Process

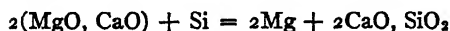
By ANDREW MAYER,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

EARLY in 1942 National Lead Co. was requested by the War Production Board to construct and operate a plant for the Government to produce magnesium by the ferrosilicon process which had been developed by Dr. L. M. Pidgeon in the laboratories of the Canadian National Research Council. A contract with the Defense Plant Corporation was concluded in May 1942 and Magnesium Reduction Co., a wholly owned subsidiary of National Lead Co., was formed to carry out this project. The capacity of the plant was rated at 10,000,000 lb. of magnesium per year, equivalent to an average production of about 14 tons per day.

THE PROCESS

The process, in brief, is as follows: The raw materials are dolomite and ferrosilicon, 75 per cent grade. The dolomite is calcined, the calcine and ferrosilicon are ground and mixed and the mixture is briquetted. The briquets are charged into tubular retorts of chrome-nickel steel set horizontally in a furnace with the open ends projecting outside the front wall. The retorts are then closed and evacuated. Magnesium is liberated according to the reaction



It is distilled from the charge and con-

densed on a removable sleeve in the throat of the retort. Sodium and potassium, if present, are also liberated, distilled and condensed on a "sodium condenser" in the end of the retort. At the expiration of the distillation period the retorts are discharged and the cycle of operations is repeated.

For the rated daily capacity of 14 tons of magnesium there are required approximately 170 tons of dolomite, equivalent to about 85 tons of calcine, and 16.5 tons of ferrosilicon. The retort residue, a bulky powder which at present is waste, amounts to about 87 tons.

CHOOSING THE SITE

The investigation to select the location of the plant was conducted by the Research Laboratories of National Lead Co. This work included geologic and economic surveys of a number of districts, examination of dolomite samples by chemical, spectrographic and petrographic methods and large-scale tests of dolomite from several of the more promising localities. In the last-named tests 2-ton samples were put through the ferrosilicon process in the pilot plant of the Canadian National Research Council, under the guidance of Dr. Pidgeon.

The conclusions drawn from the investigation, in regard to the quality of dolomite to be used in the ferrosilicon process, were: First, the dolomite should contain not less than 21 per cent MgO and not more than 2 per cent acid-insoluble material. Second, the dolomite should

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* Chief Engineer, National Lead Co., New York, N. Y.

contain less than 0.10 per cent sodium plus potassium in order to avoid more or less serious fires, due to spontaneous ignition, when the retort is opened.

As a result of the investigation it was decided to build the plant at Luckey, Ohio, on the New York Central Railroad about 14 miles south of Toledo. In this district there are large deposits of dolomite of suitable quality. Natural gas and electric power are available. In the vicinity of the site there are several lime plants from which calcined dolomite can be obtained and it was decided to purchase the calcine instead of installing facilities to produce it.

Singmaster and Breyer, New York, was engaged as architect-engineer and United Engineers and Constructors, Inc., Philadelphia, was engaged as constructor.

THE PLANT

Construction was started in June 1942. A production control unit, housing a furnace with four full-sized retorts and small-scale auxiliary equipment, was completed in October and initially was operated to train personnel. Plant production was started on Dec. 30, 1942, about six months after ground was broken.

The general plan of the plant is shown in Fig. 1.

Water is pumped from deep wells on the site. Electric power is purchased.

Process fuel is natural gas with a calorific value of about 1025 B.t.u. The plant is heated by steam from coal-fired boilers in a central boiler house.

Steel was conserved as much as practicable in construction on account of emergency conditions.

Equipment and Operations

The flowsheet of the plant is shown in Fig. 2. Calcined dolomite, calcined in coal-fired shaft kilns, ground in a hammer

mill and screened through 16 mesh, is received in a closed-body dump truck in 12-ton lots from the near-by plant of the National Gypsum Co. Specifications are: acid insol. not more than 0.5 per cent; CO₂ not more than 0.75 per cent. The content of combined water is about 0.25 per cent in winter and 1.25 per cent in summer. The calcine is used without further grinding. Screen analyses are given in Table 1.

TABLE 1.—Screen Analyses of Feed
PER CENT

Mesh	Calcine	Ground Ferrosilicon
+30	21	0.2
+50	40	1.7
+100	48	10.0
+200	56	31.0
-200	44	69.0

Briquetting

The arrangement of the briquetting presses, which are of the roll type, is shown in Fig. 3. Each precompression press has a feeder consisting of a casing provided with rotary arms, which force the material down into the roll pockets. The pockets of the finishing presses are lubricated by a fine spray of mineral oil. Operating data are given in Table 2.

The precompression presses are recent additions. Previous to their installation briquetting was a single-stage operation.

TABLE 2.—Briquetting Data

Item	Precompression	Finishing
Feed, lb. per hr.		9,000
Briquet production, lb. per hr.		6,500
Feeder speed, r.p.m.	40 to 80	
Feeder power input, kw.	12 to 15	
Roll speed, r.p.m.	10	7
Roll power input, kw.	25 to 30	25 to 35
Approximate operating time, press-hr. per day.	24	35

The average density (grams per c.c.) of the briquets is about 2.15. They are packed in paper bags, each containing

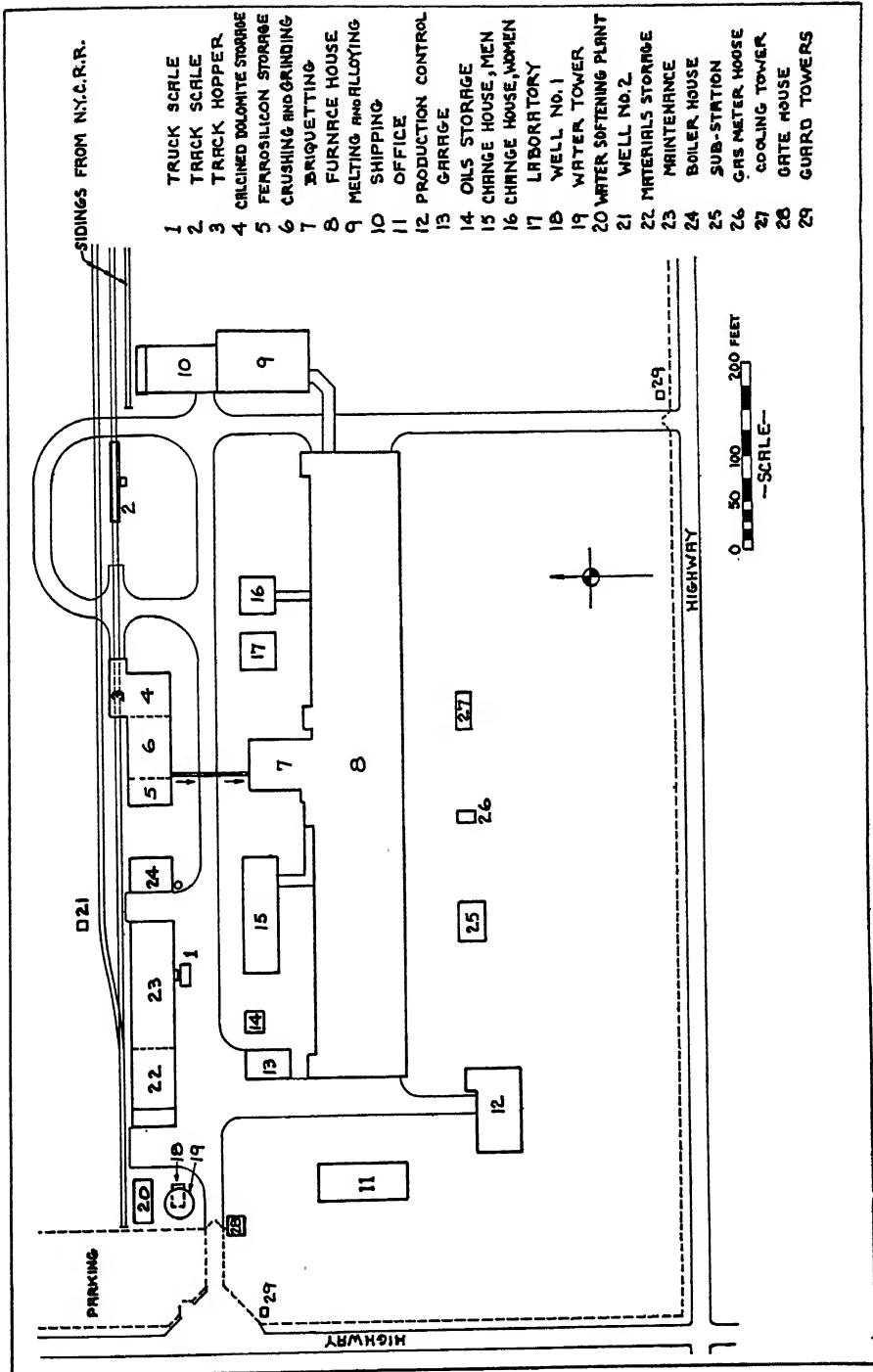


FIG. 1.—GENERAL PLAN OF PLANT.

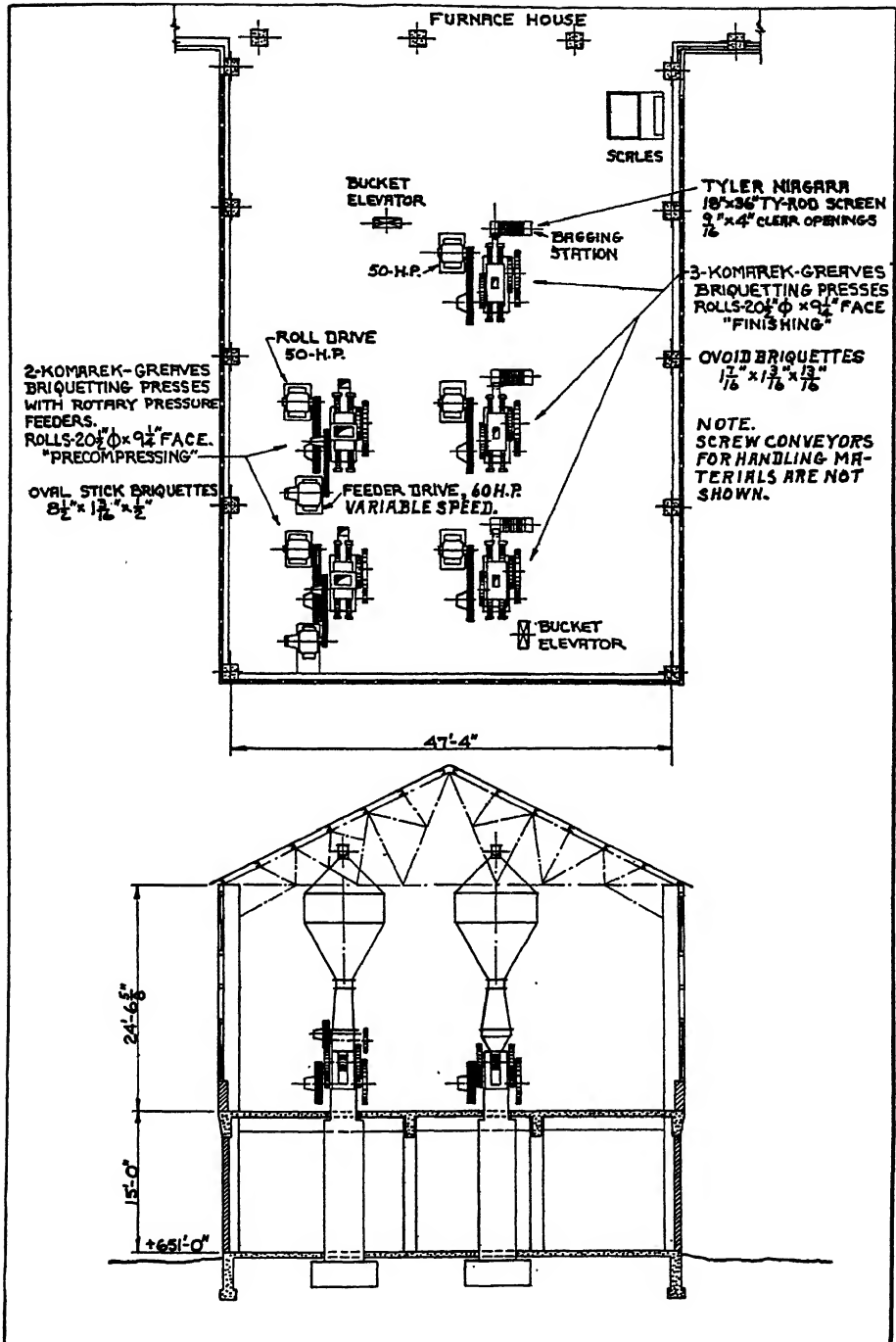


FIG. 3.—BRIQUETTING WING.

45 to 50 lb. The finishing presses and the packing of briquets are shown in Fig. 4.

No suitable binder for the briquets

installed ahead of the briquetting presses but at present the operating details have not been worked out.

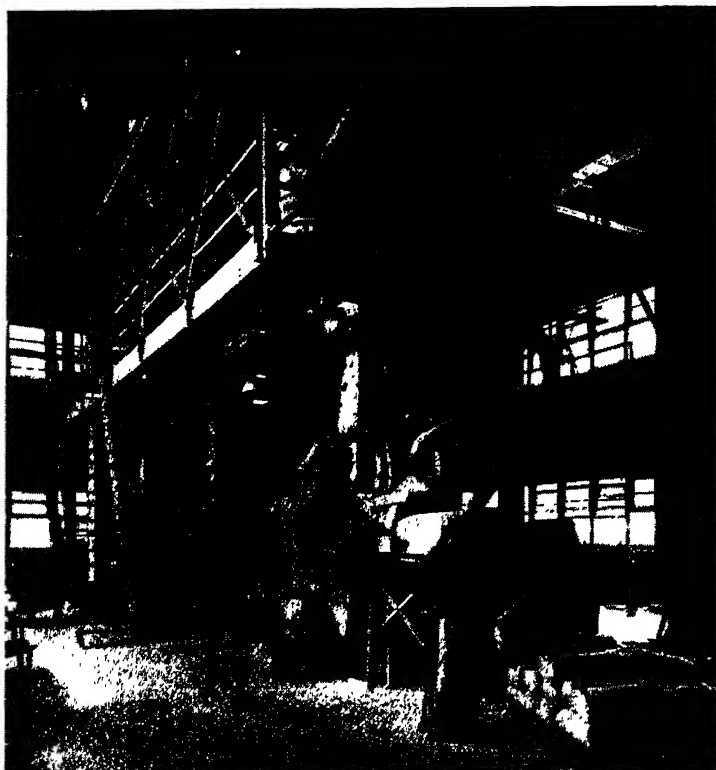


FIG. 4.—FINISHING PRESSES AND PACKING OF BRIQUETS.

has been found. The production of strong briquets, which are essential for efficient operation of the process, has been a difficult problem, involving high power consumption and excessive maintenance costs. Two-stage briquetting and comparatively coarse calcine, such as that in use, are decidedly helpful. A finer calcine is preferable if the mix can be briquetted successfully.

It has been found by experiment that ball-milling the calcine-ferrosilicon mixture with comparatively large balls materially improves its briquet-making properties. In line with these experiments a tube mill, 7 ft. by 23 ft. 9 in., has recently been

Retort Furnace and Auxiliary Equipment

The retort and fittings are shown in Fig. 5. Compositions in use for the alloy-steel body are: 35 Ni, 15 Cr; 28 Cr, 20 Ni and 28 Cr, 15 Ni. In each retort the butt, alloy tube and connecting weld metal are nominally of the same composition. The alloy tube is welded to the seamless steel tube with 25 Cr, 20 Ni welding rod. Both static and centrifugal alloy tube castings are in use.

The retort furnace is shown in Figs. 6, 7 and 8. The walls are sheathed with $\frac{3}{8}$ -in. Transite, not shown in the drawings.

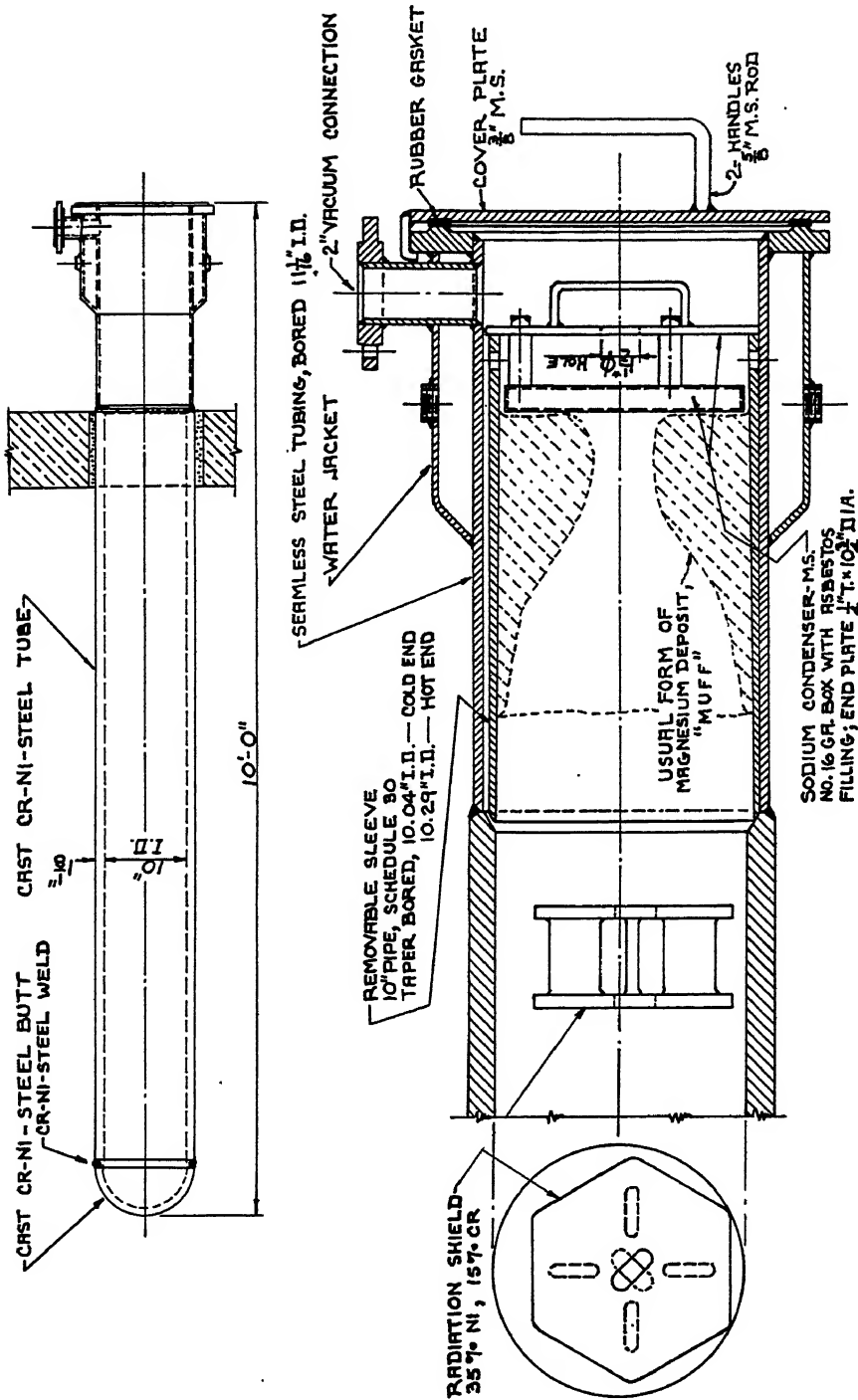


FIG. 5.—RETORT AND FITTINGS.

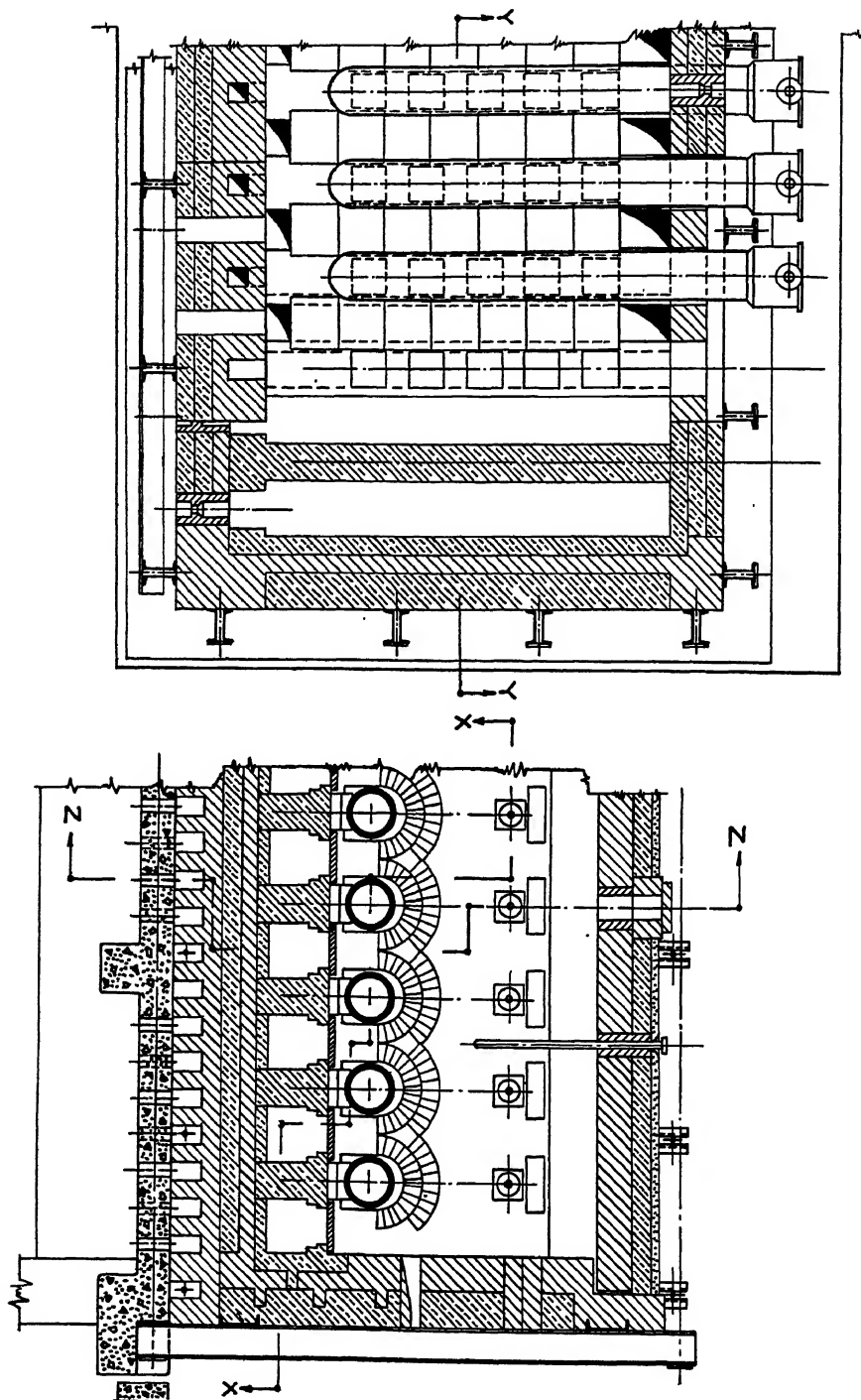


FIG. 6.—RETORT FURNACE.
Sectional plan on X — X, Fig. 7.

FIG. 7.—RETORT FURNACE.
Section on Y — Y, Fig. 6.

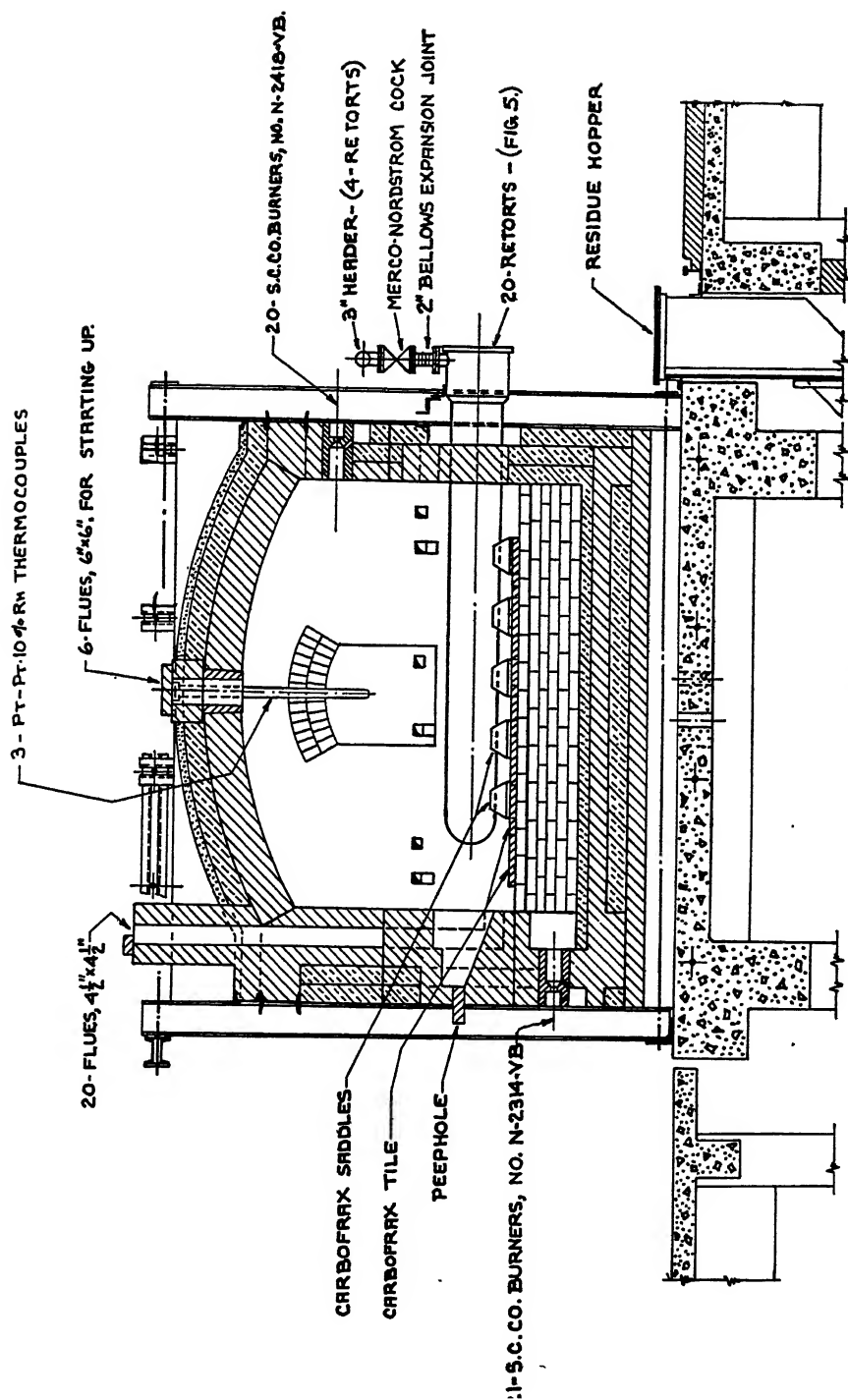


FIG. 8.—RETORT FURNACE.
Section on Z — Z, Fig. 7.

The furnace is fired by low-pressure velocity burners made by Surface Combustion Co., which are supplied with air at 20 oz. pressure by a Spencer turboblower.

ing recording controller, which regulates the gas flow to the top burners (Fig. 8). The bottom burners are adjusted manually when the furnace is started and thereafter

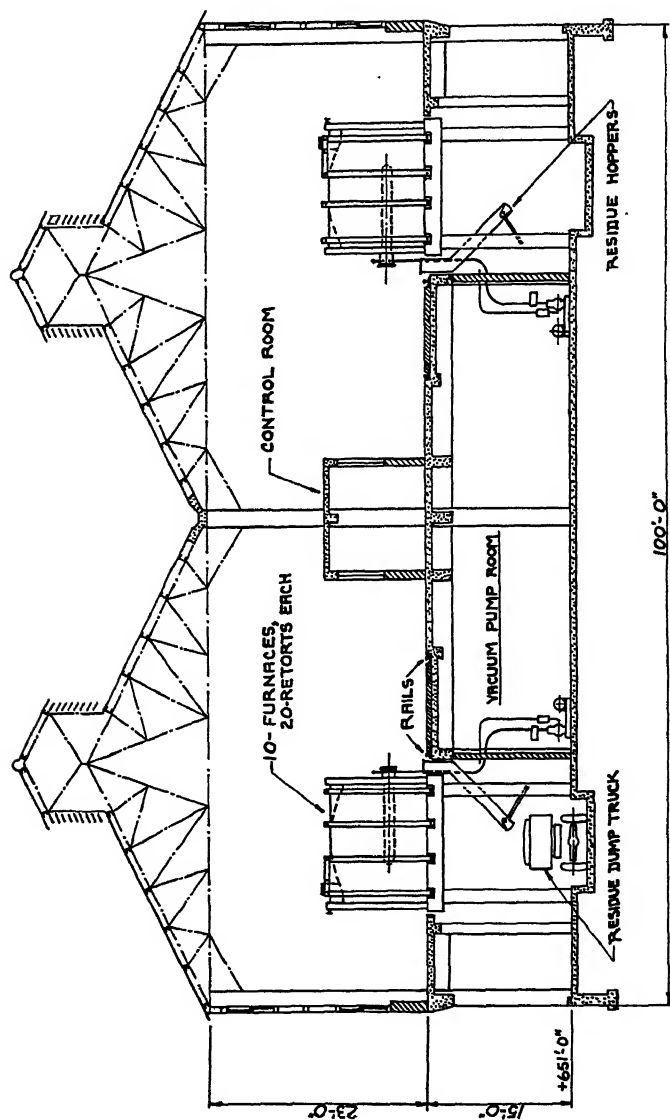


FIG. 9.—CROSS SECTION OF FURNACE HOUSE.

There are three zones of temperature control, one in the middle and one at each end. The temperature of each zone is controlled by a Bristol pneumatic indicat-

the gas flow to them is virtually constant, under normal operating conditions. The gas flow to both top and bottom burners is reduced automatically if the furnace

temperature should become excessive and is shut off automatically if the supply of 20-oz. air should fail.

The vacuum system of the furnace

There is a vacuum recording system for each furnace, which includes a National Research Corp. high-vacuum thermocouple gauge for each group of four retorts and

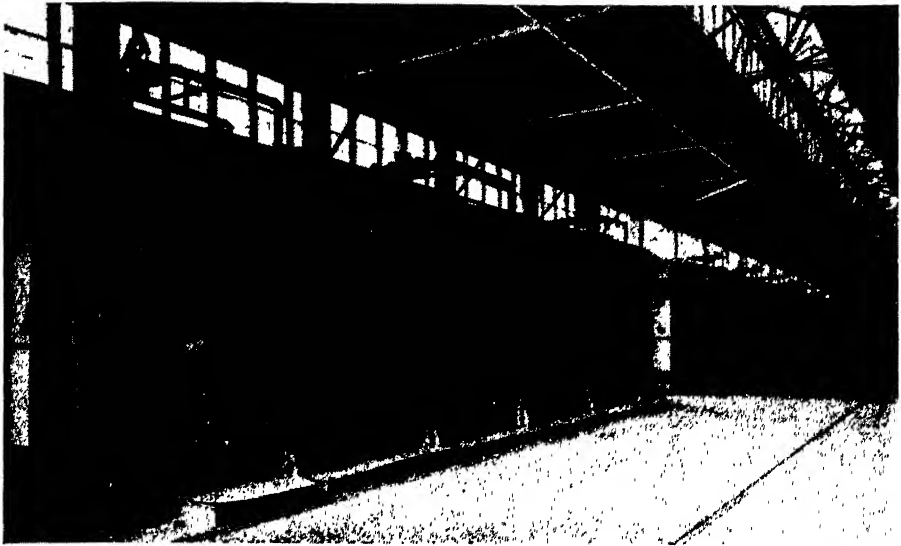


FIG. 10.—RETORT FURNACES.

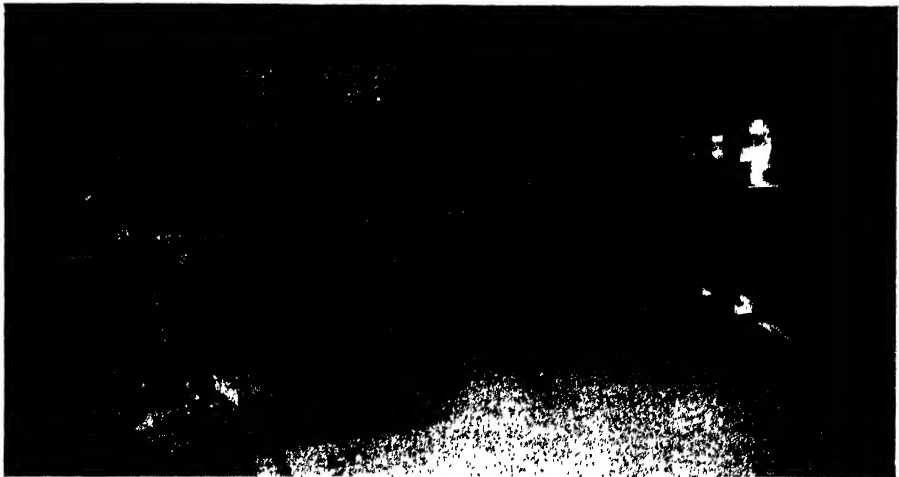


FIG. 11.—MACHINE FOR DISCHARGING RETORTS.

includes five Kinney mechanical vacuum pumps, each connected to a group of four retorts (Fig. 8). Each pump is rated at 100 cu. ft. per min. and each is protected by a Staynew filter. All valves are Merco Nordstrom plug cocks.

a Leeds and Northrup five-point recording potentiometer. Vacuum is indicated by Stokes portable McLeod gauges.

Fig. 9 is a cross section of the furnace house, which indicates the arrangement of the retort furnaces and vacuum pumps

and the location of the control rooms containing the temperature controllers and vacuum recorders.

Operation of Retort Furnaces

Fig. 10 shows a group of retort furnaces. The retort cycle is 10 hours.

The average time under vacuum is about 9.5 hr. Then the vacuum is broken, the retort is opened and the fittings and condensed magnesium are removed. Most of the retort residue is discharged mechanically, a small remainder being hoed out by hand. One of the two machines for discharging the retorts is shown in Fig. 11.

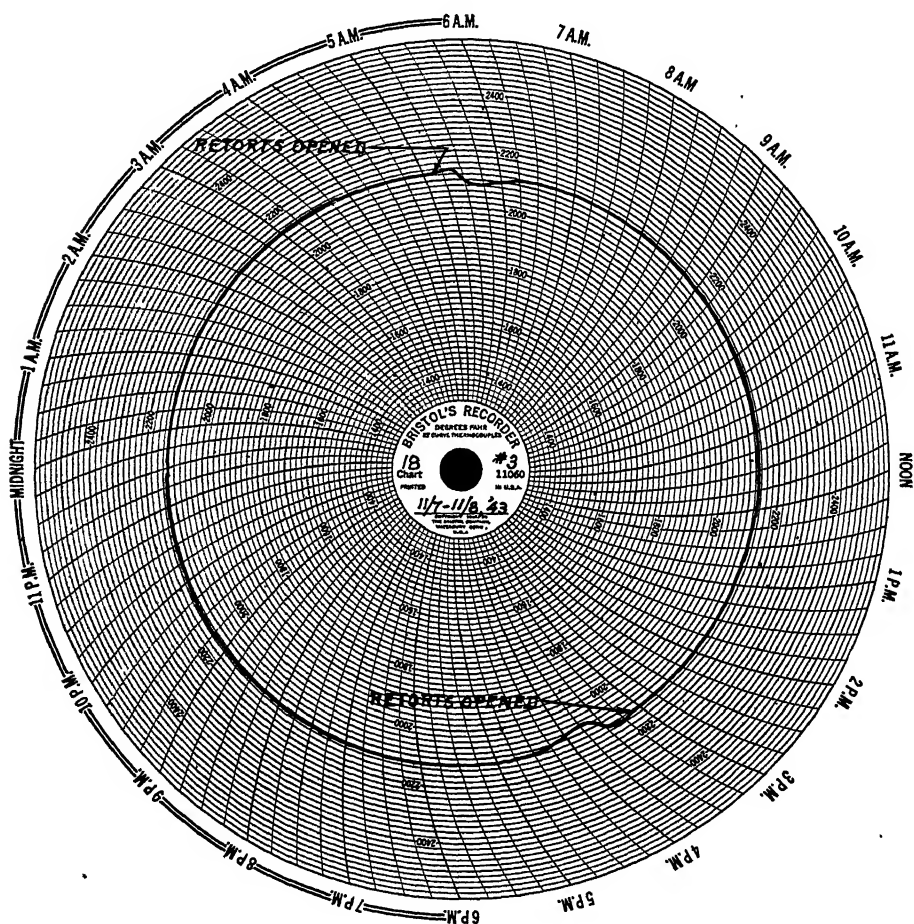


FIG. 12.—TYPICAL 24-HOUR TEMPERATURE CHART OF A RETORT FURNACE.

Five paper bags of briquets are charged into each retort by hand and the retort fittings (Fig. 5) are inserted. After a "burn-off" period of 10 to 30 min., to reduce the proportion of combined water, the retort is closed and vacuum is applied.

The two helical discharge screws are of alloy steel; 35 Ni, 15 Cr. The residue drops into hoppers from which it is loaded into a dump truck (Fig. 9) for disposal.

Average vacuum readings with the McLeod gauge are as follows:

Elapsed time, hr....	1	3	5	7	9
Microns mercury....	1000	100	60	50	45

The temperature of the furnace is so adjusted that the temperature of the retorts is 2130°F., as determined with a Leeds and Northrup optical pyrometer

Cooling water is recirculated through the water jackets of the retorts at an average rate of about 1 gal. per min. per retort. The temperature of the water and the rate of flow are not critical. Apparently the only requirement in this connection is to keep the jackets filled with water.



FIG. 13.—REMOVAL OF MAGNESIUM DEPOSIT FROM SLEEVES.

toward the end of the retort cycle. The furnace temperature may be 10° more or less than this figure. A typical 24-hr. temperature chart of a retort furnace is shown in Fig. 12. It reveals a slight rise in temperature when the retorts are opened, followed by a distinct drop upon charging, after which the temperature gradually rises to normal and is nearly constant for the rest of the cycle.

The average pressure in the furnace is 0.05 in. water and the air-gas ratio is so adjusted that the waste gases contain about 1 per cent of oxygen.

The gas consumption per furnace is 6200 cu. ft. per hour at the beginning of the cycle and 2800 at the end; 3600 average.

The sealing oil of the vacuum pump becomes slightly contaminated by dust and moisture and is replaced by clean oil previous to each cycle of its connected retorts. The "dirty" oil is reclaimed by filtering and heating.

Average production data are as follows:

Mix ratio, theoretical; that is, 28 lb. of silicon to 80.6 lb. of magnesia	
Briquets charged, lb. per retort.....	235
Magnesium recovered, lb. per retort...	31.5
Silicon efficiency, per cent.....	65

The magnesium deposit, in the form of a "muff," is driven out of the removable sleeve (Fig. 5) by a pneumatic hammer provided with a steel disk that fits inside

the sleeve. The removal of magnesium deposit from the sleeves is shown in Fig. 13.

The magnesium "muffs" are transferred to the melting and alloying department, where they are melted down and mixed with other metals by usual methods to make alloys for incendiary bombs and aircraft parts.

The plant has also produced a few lots of unalloyed magnesium ingots, of which a typical spectrographic analysis is as follows: copper, < 0.005 per cent; lead, < 0.005; iron, 0.003; nickel, < 0.005; manganese, 0.001; silicon, < 0.008.

Plant Control

The laboratory is well equipped to make such chemical and spectrographic analyses as are required in a plant of this kind.

Work is carried on continuously in the production control unit for the control and improvement of plant processes. It has proved a most valuable asset.

Retorts

Under service conditions the retorts slowly collapse and are "blown up" in place at regular intervals by compressed air at 100 pounds.

The estimated average life, including service after repairs, is about 250 days. In general, failure has been due to scaling and to cracks caused by "blowing up" after collapse had become extensive. In respect of retort life the indications are that casting and welding techniques are

more important than composition, within the limits used.

The composition specified for replacement retorts is the nominal 28 Cr, 15 Ni alloy steel containing not more than 0.30 C, 1.25 Mn and 1.50 Si. All the metal as supplied meets these specifications except for carbon, which, on account of difficulty in obtaining low-carbon ferrochrome, runs from 0.25 to 0.40.

Safety

In general, the only precautions that have been found necessary are those commonly observed in other smelting operations. There are occasional small flares when a retort is opened, or in melting down the magnesium, but these are easily extinguished and have not proved a serious problem.

Production

The present production of the plant is substantially greater than the originally rated capacity of 10,000,000 lb. of magnesium per year.

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Some Developments in the Production of Magnesium from Dolomite by the Ferrosilicon Process

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UNTIL recently, the only commercial method of producing magnesium has been fused salt electrolysis, despite a considerable amount of experimental work on the direct reduction of magnesium oxide. In this early work, a number of investigators demonstrated that magnesium oxide would react with any one of several reducing agents to produce magnesium vapor, but that the mixture of magnesium oxide and reducing agent must be heated to a high temperature even in a vacuum. In particular, it was demonstrated that silicon and aluminum are effective reducing agents and that when either of these is used the magnesium vapor can be condensed to massive metal. In spite of this knowledge, no successful commercial reduction process was developed, at least in this country, because of the operational difficulties imposed by the requirement of high temperature and vacuum and because of the high cost of the reducing agent.

The outstanding experimental work done by Pidgeon, who carefully reviewed all of the known methods of making magnesium and then selected ferrosilicon reduction, overcame some of the operational difficulties. The process developed by Pidgeon comprises briquetting a mixture of calcined dolomite and reducing agent, preheating the briquets to about 600°C. in an externally heated alloy retort, reducing the

MgO with silicon in an evacuated horizontal alloy retort heated externally to about 1150°C., and condensing the magnesium vapor to a solid in a cold extension of the retort projecting beyond the front of the furnace.

A major advantage of Pidgeon's process is that the retort is not cooled down between charges. Earlier investigators had used apparatus that necessitated cooling and reheating of the retort between charges.

Early in January 1942, when the War Production Board was considering the Pidgeon process for quickly increasing the production of magnesium, The New Jersey Zinc Co. offered to have a research investigation of the process carried on, with the hope of assisting in its further development. This offer was accepted, and a two-retort pilot plant was built at Palmerton and put in operation on Jan. 29, 1942. An intensive investigation of certain phases of the process was carried out in the ensuing four months. This investigation was completed in the last part of May 1942, and the pilot plant was then shut down.

Subsequently, The New Jersey Zinc Co. was requested to have further development work done on the process, and a more extensive investigation was undertaken in August 1942 under contract with the War Production Board and under the supervision of the War Metallurgy Committee. This paper describes the phases of the investigation that are thought to be of sufficient general interest to merit publication.

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WET BRIQUETTING

Pidgeon made briquets by mixing finely ground calcined dolomite and finely ground ferrosilicon and briquetting the dry mixture in a plunger press under very high pressure. It was planned, however, to do the commercial briquetting in a roll press. Experience with the briquetting of other materials led the investigators to fear that the briquetting of this dry material would present serious difficulties in large-scale operation. Furthermore, in several weeks experimentation it was not possible to make satisfactory dry briquets in any roll presses available at the start of the investigation. This led to experiments with wet briquetting. Sufficient water was added to slake the lime and to provide excess water in an amount that yielded a plastic mix. The excess water was then removed by drying at 110° and the water of hydration was removed by heating the charge to 600° or 700°C. in an externally heated muffle. Excellent briquets were produced by this procedure and, after several months experimentation, the following process was developed:

1. A mild calcination of the dolomite designed to yield a calcine that would hydrate readily.

2. Hydration of the calcine with about 12 per cent excess water followed by addition of the ferrosilicon and thorough mixing. This was done customarily in a pan mill with a very heavy muller. Experiments showed that satisfactory results could be obtained also in a paddle mixer or a cement mixer.

3. Densification of the mix by passage through rolls. These can be smooth rolls, corrugated rolls, or briquetting rolls.

4. Briquetting of the densified mix by passage through briquet rolls exerting a pressure of about 2000 lb. per sq. in. on the mix.

5. Removal of free water from the briquets in a drier.

6. Removal of water of hydration and preheating of the briquets in an externally fired steel tube. This tube was inclined about 45° and was 8 or 10 in. in internal diameter. The tube was fired at a temperature of 850°C. Use of a higher temperature had an adverse effect on the recoveries obtained in the subsequent reduction, presumably because of oxidation of silicon. A tube of a larger diameter was tried and found to have a lower capacity, owing to the difficulty in driving heat to the center of the charge with the limitation in firing temperature imposed by oxidation of the silicon.

7. Charging of the preheated briquets to the reduction retort.

A satisfactory alternative to steps 1 and 2 was found to be the purchase of commercial hydrated dolomite. It is believed, therefore, that the best commercial procedure would be to hydrate in conventional hydrating equipment and follow that by a mixer in which the ferrosilicon could be incorporated.

A serious drawback to this wet briquetting process in commercial operation would be low capacity of the externally fired preheaters. Experimental work was undertaken therefore to determine whether direct-fired preheating could be accomplished without either oxidation of the silicon or carbonation of the lime. It was found that by limiting the temperature of the hot gases, oxidation was avoided and that by discharging briquets at a temperature of 650° to 750°C. the CO_2 content was low. These requirements could be met easily in an internally fired rotary kiln, and it was also found that the strengths of the briquets were adequate to prevent any serious breakage due to the tumbling motion in the kiln. Most of the experimental work was done on a small batch-operated kiln, but one test was made on a 60 by 6-ft. rotary kiln, with satisfactory results. The capacity of the 60-ft. kiln was found to be in

excess of $2\frac{1}{2}$ tons per hour of dry briquets, which makes this method of preheating far simpler and cheaper than preheating in indirectly fired muffles.

The dolomite used in the early work on wet briquetting was of the type in which only the calcium oxide hydrates. With such a dolomite the density of preheated briquets obtained in the process is about 1.7 grams per cubic centimeter. Later in the work, some dolomites were encountered in which part or all of the magnesia also hydrates. The hydration of the calcium oxide absorbs about 16 per cent water, and the hydration of all the magnesia absorbs about 8 per cent additional water. The complete hydration of the magnesia results in a decrease in the density of the preheated briquet from about 1.7 to 1.3 grams per cubic centimeter.

Since it is important to get as much weight of charge in a retort as possible, any decrease in briquet density is undesirable. Means of avoiding hydration of the magnesia were, therefore, sought. It was found that by hard-burning the dolomite in the calcining step, hydration of magnesia could be retarded. This expedient could not be utilized, however, because hydration then continued in the finished briquets and caused their cracking and disintegration. Similarly, hydration could be limited by limiting the amount of water to that required to hydrate the calcium oxide, then adding the excess water just before briquetting. This also led to hydration of the magnesia in the finished briquet, with resultant disintegration of the briquet.

Addition of various substances to the dolomite prior to calcination was tried in the hope of inhibiting hydration of the magnesia. Preliminary results indicate that the use of 1 per cent sodium chloride or calcium chloride at least partially inhibits hydration of magnesia and thus partially avoids the decrease in density. Further work on this possibility is in progress.

DRY BRIQUETTING

As mentioned before, we were unable to produce usable briquets from the dry mixture of calcined dolomite and ferrosilicon in any roll press available to us during the first part of our investigation. During this period some information about dry briquetting was obtained by use of a cylindrical mold and plunger operated in a hydraulic press. In November 1942, a Komarek-Greaves press was borrowed from the Ford Motor Co. A systematic study of dry briquetting was then made, utilizing both this roll press and the plunger press.

The Komarek-Greaves press is a high-pressure roll press designed for briquetting dry materials. It employs two alloy-steel briquetting rolls of $20\frac{1}{2}$ -in. diameter by $9\frac{3}{16}$ -in. face and produces almond-shaped briquets of a size $1\frac{5}{16}$ by $1\frac{1}{4}$ in. by 1 in. thick. To obtain the required briquetting pressures, a load of about 100 tons is applied to each roll by means of springs. The spring assembly is held by two rods extending through the frame and the spring tension is controlled by adjusting two nuts that hold the spring assembly in place. The rolls are gear-driven at 6 to 9 r.p.m. by a 40 to 50-hp. motor, and a fine oil spray on the rolls facilitates the discharge of the briquets from the pockets. The briquets are discharged from the press on to a moving belt, at the end of which there is a screen to remove the fines.

The material to be briquetted is fed to the press by a mechanical feeder that is independently driven by a variable-speed 40 to 50-hp. motor. The feeder, directly above the briquetting rolls, consists of six radial arms rotated on a shaft parallel to the briquetting-roll shaft. Two screw-shaped blades force the material from the sides to the center and the arms compress the material and force it into the briquetting rolls. The speed of the feeder is varied from 40 to 90 r.p.m., depending on the type and particle size of calcine briquetted. The

output of screened briquets is $2\frac{1}{2}$ to 3 tons per hour.

The size of the briquet produced on the press is fixed by the shape and size of the pocket and by the amount the rolls separate during briquetting. The separation of the rolls even under maximum spring tension produces a fin, which for the $15\frac{1}{8}$ by $1\frac{1}{4}$ by 1-in. briquet is approximately $\frac{1}{4}$ in. thick. It was felt that improvements in briquetting could be realized by reducing the thickness of the fin. An attempt to accomplish this was made by substituting solid blocks for the springs, but only a partial reduction in fin thickness was obtained.

The production of usable dry briquets even with the Komarek press is a difficult matter. The principal drawback in briquetting is the fact that the present roll press is working too near the limit of its capacity in handling the power input necessary to produce a briquet of good strength. The operating load must be limited to avoid excessive maintenance and roll breakage.

A number of interrelated variables influence the quality of the briquets, and optimum values that are universally applicable do not exist for each of these variables. Variables found to be important are the nature of the dolomite, the method of calcining, the size to which the calcine is crushed, the method of operating the feeder and press, and the moisture and CO_2 content of the briquets.

The one invariably important requirement is the maintenance of low moisture and CO_2 content. If these are allowed to be above 1 per cent in the briquets as they are charged to the retorts, disintegration of the briquets occurs during the reduction treatment. This disintegration becomes increasingly severe as the moisture and CO_2 content increase. The presence of the resultant fine material has a marked adverse effect on the speed and completeness of the reduction reaction.

The other variables influencing briquet-

ting are so interrelated that all must be considered together. All that will be attempted in this paper is to state the general range of conditions found to give the best results and to make a few qualitative observations about the effect of varying some of the conditions.

A practice that has been found to yield briquets that will withstand mechanical handling and reduction treatment with minimum breakage and disintegration is as follows:

1. A medium-burned calcine having an ignition loss (CO_2 and H_2O) of not more than 0.5 per cent and ground to at least 80 per cent through 100-mesh screen.
2. Ferrosilicon of at least 75 per cent silicon content.
3. Preliminary grinding of the ferrosilicon to pass 65 mesh, followed by grinding the calcine and ferrosilicon together in a ball or rod mill, which increases bulk density of the mix.
4. Feeding the milled mix to the Komarek-Greaves roll press with a feeder speed regulated to produce the maximum safe briquetting pressure.
5. Operation of the press at a slow speed (6 to 9 r.p.m.) to permit maximum time of pressure application on the briquets.
6. Screening of the briquetted material to remove the broken briquets and fines.
7. Storing of the briquets in airtight containers or prompt charging to the retorts to prevent absorption of moisture with consequent disintegration.

Some of the variables affecting briquetting and reduction operation are:

1. A mild-burned calcine is easier to grind and briquet than a hard-burned calcine. However, the mild-burned material absorbs moisture at a faster rate and also the briquets disintegrate during the reduction operation to a greater extent. Briquet density increases with temperature of calcination, which permits increased charge burdens and magnesium production.

The best all-around results have been with a medium-burned calcine.

2. A finely ground mixed charge of which 80 to 90 per cent passes a 200-mesh screen produces the strongest briquet. However, a mix of this fineness is more difficult to briquet because of the difficulty in forcing sufficient feed into the pockets to form the briquets.

3. Ball or rod-milling of the mixed charge increases the bulk density 25 or 30 per cent. The power requirements on the press feeder greatly decrease with increased bulk density of the mixed charge and better briquets are produced.

4. The most uniform briquetting conditions are attained with two presses in series. The first press is equipped with a feeder and on this unit operated at high speed a densified material is produced. The densified mix is fed to a second press without a feeder. This, however, involves the use of two presses requiring high power consumption and high maintenance.

5. Laboratory tests on briquets made with a cylindrical mold, plunger, and hydraulic press have shown that the inherent briquetability of calcines may vary widely, depending on the nature of the dolomite.

6. Resistance of briquets to the heat shock incident to charging into a hot retort is an important property of briquets. On the basis of laboratory tests, the following statements can be made:

- a. High-temperature calcine briquets are definitely more resistant to heat shock than low-temperature calcine briquets.
- b. Aging of calcine or aging of briquets impairs resistance to heat shock. High-temperature calcination mitigates this effect of aging.
- c. Fine mix briquets are poorly resistant to heat shock.
- d. Briquets, in general, are more resistant to heat shock at 1150° than at 1000° or 850°C.

It has been found possible to make usable briquets under the conditions already described provided the size of the briquets is small. The general practice has been to use an almond-shaped briquet about 1½ in. by 1¼ by 1 in., which weighs about 30 grams. Recent work has indicated that a briquet of usable quality can be made more readily if a still smaller size, weighing about 17 grams, is used. This briquet suffers less breakage during handling and is less prone to disintegration during the reduction treatment.

The established dry briquetting procedure yields a briquet having a density of about 2.0 grams per c.c. with most dolomites. It has been found that addition of from 1 to 5 per cent fluorspar to the dolomite prior to calcination profoundly influences the nature of the calcine and makes it possible to attain a briquet density of about 2.5 grams per c.c. This permits a proportional increase in the weight of briquetted material which can be charged to the retort and, under the normal operating cycle, with some dolomites may lead to an increase in magnesium yield of nearly 25 per cent. The fluorspar addition also makes the calcine less susceptible to absorption of moisture and CO₂. This should be of practical importance in plant operation, since it should decrease disintegration of briquets during the reduction treatment.

COMPARISON OF WET AND DRY BRIQUETTING

Only the dry briquetting method has been used in commercial practice, so that it is not possible to state with positiveness which method is preferable. The advantages and disadvantages of each method can be summarized, however.

The disadvantages of wet briquetting are the necessity of a hydration step, a pre-heating step, and a lower density briquet resulting in a lower charge weight in the retort.

The advantages of wet briquetting are simpler and less expensive briquetting with high press capacity, production of a much stronger briquet of any desired size, freedom from disintegration of the briquets during reduction. The consequent absence of fines in the retort charge makes it feasible to obtain more complete utilization of silicon and to use a shorter reduction cycle.

The disadvantages of dry briquetting are a difficult and expensive briquetting operation with low press capacity, a relatively weak briquet of small size, and a strong tendency to form fines in the charge due to the weakness of the briquets and to their tendency to absorb moisture and CO_2 . The presence of fines in the charge causes less efficient utilization of silicon and lower yields of magnesium per unit weight of charge.

The outstanding advantage of dry briquetting is the higher briquet density, which permits higher charge weights and greater magnesium yield per retort.

Earlier in the investigation it seemed that, taking all factors into consideration, the wet briquetting method was preferable. In view of the recent experience with the very small dry briquets and, particularly, the discovery that dry briquet densities in excess of 2.5 grams per c.c. can be attained by use of fluorspar, the investigators are inclined under most conditions to favor dry briquetting.

REDUCTION TREATMENT

Reduction tests were made in a block of four individually oil-fired retorts. Direct contact of the oil flame on the retort was avoided by means of a shelf placed below the retort. By this means complete combustion of the oil was accomplished before the combustion gases passed upward through openings in the shelf into the retort chamber. The retorts were of the standard 10-in. i.d. alloy-steel type with 5 ft. of their length in the heated zone.

Each retort was connected to a Stokes mechanical vacuum pump of 28 or 50-cu. ft. capacity, so that individual operation was possible.

Charging and discharging of the retorts was done manually. Charging of wet-process briquets involved handling hot preheated briquets at about 700°C . and these were weighed in buckets, deposited on a trough, and pushed into the retort. The retorts were connected to the vacuum line immediately after charging was completed. The dry briquets were normally charged cold and were weighed out and charged in paper bags to facilitate handling and to avoid breakage.

With unpreheated dry-process briquets, the retorts were left open for 15 to 25 min. prior to evacuation, to burn the paper bags and any oil adhering to the briquets. Residue from the retorts was discharged over a $\frac{1}{2}$ -in. grizzly to determine the amount of fines that served as an index of the degree of disintegration of the briquets during reduction.

Vacuums of 200 to 250 microns of mercury in 1 to $1\frac{1}{2}$ hr., and final vacuums of 50 to 100 microns were considered to be satisfactory. These conditions were not obtained unless the briquets were low in CO_2 and H_2O and the vacuum pumps in good operating condition.

Most of the reduction tests were made with a mixture of chemically equivalent proportions of calcine and 75 per cent grade ferrosilicon. This mix was chosen as representing the most satisfactory compromise between yield and efficient utilization of silicon. The charge weight with wet-process briquets averaged 120 lb. and with dry-process briquets the average weight was 140 pounds.

At the end of each run the retorts were opened and the sleeves containing the massive magnesium were removed before the residue was extracted.

With the wet-process briquets the silicon efficiencies obtained were 70 to 75 per

cent in $7\frac{1}{2}$ hr. at vacuum at 1150°C . temperature. At a 1225°C . temperature, silicon efficiencies of 78 to 80 per cent were obtained in $7\frac{1}{2}$ hr. at vacuum. Under optimum conditions, comparable efficiencies were obtained with dry-process briquets. The operating plants have been unable to maintain the optimum conditions with the dry-process briquetting and therefore have not obtained these high efficiencies.

It has become standard practice to express the completeness of the reduction reaction in terms of the percentage utilization of silicon, since this is the more expensive ingredient. This is called silicon efficiency, and is calculated from the weight of silicon in the charge and the weight of magnesium collected.

Laboratory tests referred to throughout this paper were conducted in a small reduction unit duplicating the essential features of a commercial unit. An alloy tube of 5 in. i.d. and having a 2-ft. immersion in a Globar-heated furnace was used for reduction of a briquetted charge weighing about 950 grams. The briquet charge occupied only the uniform temperature zone of the retort. Temperature, in general, was measured outside the retort and at the midpoint of the uniform temperature zone, and was so regulated as to maintain an inside operating temperature of 1150° .

The vacuum attained in this unit was about 200 microns or less. The magnesium metal was condensed in a sleeve in the cold end of the retort, producing a deposit of the usual structure and purity.

With the equipment described, and under standardized operating conditions, the laboratory unit furnished 6-hr. reduction results in excellent agreement with those obtained on the pilot-plant unit. Results were for the most part in quantitative agreement. In other cases, excellent correlation existed.

Judging by experience with the high-temperature reduction of other metals, it

was anticipated that the shape and size of the briquets would have an important influence on the time required to carry out the reduction reaction. Tests were made therefore with briquets varying in size from about $\frac{1}{2}$ in. to about 2 in. Variation of briquet size within this range did not have any marked effect on the efficiencies and yields obtained in the normal reduction cycle, although the larger briquets showed some advantage in shorter cycles. It was found, however, that the presence of fines either introduced with the charge or formed by disintegration of briquets during reduction had a marked adverse effect on efficiency and yield. The latter effect is illustrated by the data in Table 1.

TABLE 1.—*Effect of Fines in the Retort*

Charge	Furnace Temperature, Deg. C.	Percentage Loss on Ignition	Silicon Efficiency, Per Cent	Fines in Residue, Minus $\frac{1}{2}$ -in. Screen, Per Cent
a	1150	<.50	72	10-15
b	1150	1.0-2.0	62	25-40
a	1225	<.50	80	10-15
b	1225	1.0-2.0	70	30-40

a. Charge composed of whole, freshly made briquets.
b. Whole briquet charge aged for 24 to 30 hours.

The effect of degree of vacuum maintained in the retort was studied in the laboratory furnace. Variation from 0.1 mm. of mercury to 20 mm. was obtained by partly closing the valve in the vacuum line. The data in Table 2 show that

TABLE 2.—*Effect of Pressure on Efficiency*

Pressure, Mm. Hg.	Percentage Weight Loss of Charge	Silicon Efficiency, Per Cent
0.1	12.2	72
1.0	12.6	74
2.0	13.3	75
4.0	13.2	75
7.0	13.2	76
10	12.9	73
15	11.4	68
20	8.4	46

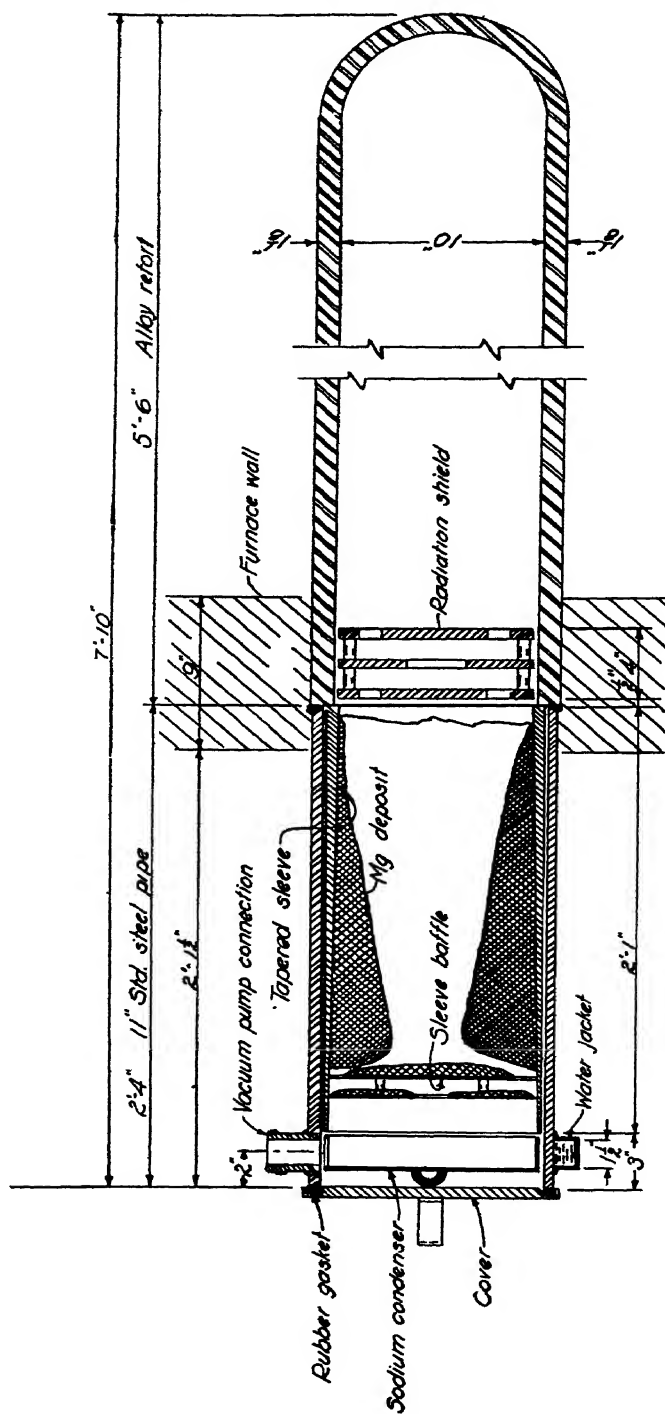


FIG. 1.—RETORT AND CONDENSER ASSEMBLY.

pressures up to 10 mm. had no significant effect on efficiency.

The composition of gas obtained in the retort in these tests is not known but is thought to have been largely hydrogen. Another test was made in which air was allowed to leak into the retort at the rate of 200 c.c. per min., which resulted in a pressure in the retort of 0.48 mm. This air leakage had no effect on the reduction of magnesium in the charge but did oxidize some magnesium vapor.

Regardless of the effect of degree of vacuum on reduction, it is necessary to maintain a vacuum of 0.1 to 0.3 mm. in order to obtain a dense metal deposit in the condenser. With increased pressure the condensed metal becomes more porous, with resultant tendency to burn and with increased losses during the subsequent melting step.

A large number of tests were made in which dry-process briquets were preheated before charging to the reduction retorts. These tests failed to show any increase in magnesium yield although there was some improvement in quality of metal as compared with unpreheated briquets containing more than about 1.0 per cent water. The chief disadvantage in preheating the dry briquets lies in the inherent weakness of the briquet, which makes it impossible to produce a preheated charge that does not contain a large percentage of broken briquets and fines. Since this has been shown to be detrimental to yield, it is felt to be more advantageous to attempt to produce a briquet low in CO_2 and H_2O directly from the briquetting operation rather than to attempt to prepare a briquet of sufficient strength to withstand the additional step of preheating.

The effect of furnace temperature on retort life and metallurgical efficiencies was studied. The early work was at furnace temperatures of 1150°C . for cycles of 8 to 10 hr. under vacuum. Later it was found that furnace temperatures

of 1225°C . could be maintained without seriously affecting the alloy retorts and at this temperature the reaction took place at an accelerated rate, as indicated by the data in Table 3.

TABLE 3.—*Effect of Time and Temperature on Reduction in 10-inch I.D. Alloy Retort*

Hours under Vacuum	Silicon Efficiency, Per Cent	
	1225°C .	1150°C .
10	80	75
8	78	73
6	75	70
5	73	66
4	69	60

Ferrosilicon can be produced with any desired silicon content but production difficulties increase with increasing silicon content, with the result that cost per unit of silicon becomes higher as the silicon content of the alloy is increased. The influence of the grade of ferrosilicon on efficiency of utilization of silicon is shown in Table 4. These results were obtained in the laboratory apparatus. Similar results were obtained in the pilot plant. It will be noted that efficiency of utilization of silicon and yield of magnesium improve with increasing silicon content of the ferrosilicon until a silicon content of 85 per cent is reached. The investigators have no explanation of the decrease in efficiency with still higher silicon contents. The selection of the optimum silicon content must be based on a consideration of both price and performance. Most of the work has been done with the 75 per cent grade.

Many materials were tested in the laboratory reduction apparatus to determine whether their inclusion in the calcine-ferrosilicon mix might catalyze the magnesium reduction reaction. Although possible catalytic effect was not always in mind, the following additions to the mix were tried: CaF_2 , MgF_2 , NaF , LiF , CaCl_2 , SiO_2 , TiO_2 , Al_2O_3 , Fe_3O_4 , Co_2O_3

and Ni_3O_4 . Only CaF_2 and MgF_2 showed catalytic effects. Many of the others caused pronounced decreases in recovery of magnesium.

Magnesium fluoride in amount of 1 per cent was effective with one dolomite and increased silicon efficiency by 4 to 5 per cent. Other dolomites did not respond favorably.

TABLE 4.—*Influence of Grade of Ferrosilicon Dry Mix, Stoichiometric Proportions, Reduction for Six Hours at 1150°C.*

Test No.	Silicon in Ferrosilicon, Per Cent	Silicon Efficiency, Per Cent	Quantity Mg. per 100-lb. Mix, Lb.
1	49.9 ^a	53	9.9
2	75.6 ^a	70	14.1
3	75.5	72	14.7
4	78.9	75.5	15.4
5	85	82	17.3
6	91.3 ^a	80.5	16.8
7	91.9	79	16.9
8	97.6 ^a	75	15.5

^a Tests 1, 2, 6, and 8 were made earlier than the other tests. A different dolomite and a different method of temperature control were used. All results are reasonably comparable, however, as can be seen by comparing Tests 2 and 3 or 6 and 7.

Calcium fluoride, either as C.P. CaF_2 or 98 per cent or 95 per cent grade fluorspar, was effective in many cases. Its effectiveness was limited to calcines of certain dolomites or to calcines that, for reasons to be noted, failed to furnish normal magnesium recoveries. The statements following apply to cases in which benefit attended its use.

Increase in fluorspar addition from 1 to 10 per cent was accompanied by progressive increase in silicon efficiency. Additions beyond about 5 per cent do not appear worth while. The results in Table 5 show

TABLE 5.—*Effect of Additions of Fluorspar*

Fluorspar Addition, Per Cent	Silicon Efficiency, Per Cent	Mg. Yield, Lb. per 100-lb. Mix
0	70	14
1	71	14.3
3	74	14.7
5	78	15.0
10	81	14.8

the effect of additions of fluorspar to a particular dolomite as determined by the standard laboratory test at 1150°C.

Pilot-plant tests substantiated the results of laboratory tests. Fluorspar substantially increased the magnesium yield from the calcine for which laboratory results are given in Table 5.

Another calcine being used in a magnesium plant showed poor performance as a result of aging, with attendant moisture pickup to a value between 1.5 and 2.0 per cent. Excessive formation of fines in the retort resulted. Reduction of the calcine was restored to normal by the addition of 5 per cent fluorspar, in spite of the fact that disintegration of the briquets still occurred. This is illustrated by the data in Table 6.

TABLE 6.—*Pilot-plant Test of Fluorspar*

Calcine	Fluorspar, Per Cent	Time at Vacuum, Hr.	Silicon Efficiency, Per Cent		Mg Yield, Lb. per 100-lb. Charge	
			1150°C.	1225°C.	1150°C.	1225°C.
Fresh	0	7½	72	79	14.4	15.8
Fresh	5	7½	72	79	13.6	15.0
Aged	0	7½	66	73	13.2	14.6
Aged	5	7½	72	81	13.7	15.4

Experience in this investigation indicates that a 5 per cent addition of fluorspar may cause more or less slagging difficulty in the residue if the temperature of operation exceeds 1150°. Residues of fluorspar-bearing mix spontaneously disintegrate to powder during cooling, owing to the mineralizing action of CaF_2 on the dicalcium silicate inversion.

The technical advantage of the use of aluminum as a reducing agent instead of ferrosilicon was demonstrated by laboratory tests on aluminum powder, aluminum-silicon alloys and various aluminum scraps. The typical results in Table 7 were obtained in comparison with ferrosilicon. In each case the test was made in accordance with standard laboratory procedure using

equivalent ratio mix and reducing at 1150° . Pilot unit reduction tests on the

TABLE 7.—*Reduction with Aluminum*

	Pure Al Pow- der	Al Turn- ings, 93.3 Per Cent Al	Al Alloy (46 Per Cent Al, 48 Si, 3 Ti)	75 Per Cent Grade Ferro
Efficiency of reducing agent, per cent.....	89	83.5	79	71
Mg per 100-lb. charge, lb.....	18.1	17.7	16.3	14.3
Mg per 100-lb. reduction agent, lb.....	120	105	116	94
Briquet density, grams per c.c.....	1.96	1.94		1.98

aluminum turnings confirmed the advantage of aluminum over silicon as a reducing agent.

Laboratory evaluation of a 70 per cent Al, 20 per cent Si alloy indicated an aluminum alloy of this composition to have a temperature advantage of 30° to 40°C. over ferrosilicon as a reducing agent at 1150°C. The time advantage of the aluminum alloy over ferrosilicon at 1150° was even more striking. It is questionable whether these findings would be quantitatively reproduced by pilot unit tests because of the difference in availability of heat under the two test conditions. Considerable advantage for aluminum over silicon, however, is accepted.

Effects of calcination treatment, milling treatment and calcine and briquet aging on the reduction reaction were investigated.

An extensive series of laboratory tests was made on each of two dolomites (one crystalline, the other amorphous) to determine the influence of each of these variables. Rotary-furnace calcines were made at 950° , 1100° and 1250°C. , the calcine-ferrosilicon mix of each was milled to 30, 60, and 90 per cent minus 200-mesh and each mix was subjected to the laboratory reduction test. The effects of aging of calcine to 4 to 5 per cent H_2O plus CO_2 pickup before briquetting, as well as the aging of briquets

protected from the atmosphere, were also determined for each of the combinations of calcination and milling conditions.

Silicon efficiencies for each dolomite under each of the many combinations of conditions were well within the limits of experimental error. For example, almost all the silicon efficiencies for one of the dolomites fell within the limits of 69 and 72 per cent. This is taken to mean that magnesium recovery is independent of all the variables investigated within the wide limits covered as far as inherent chemical reactivity of the mix reactants is concerned. The conclusion, however, probably is of academic interest only, since it is true that all of the factors affect the briquet quality more or less importantly and that magnesium recovery is dependent upon that quality in plant reduction. Briquet quality is practically without importance in the laboratory test, since the briquet charge is subjected to little handling and no fines are formed with any briquets.

While calcine aged to 4 to 5 per cent H_2O plus CO_2 did not decrease recovery even without preheating, good vacuum was more slowly attained and the metal deposit was not as good physically as that produced from low-volatile briquets. The commercial use of such high-volatile briquets would probably be disastrous, since the resultant poor quality of the briquets would seriously decrease recovery of magnesium.

RETORTS

The normal life of the alloy retorts is too long to permit very extensive tests in the four-retort pilot plant. Most of the progress on retort design and alloy composition has been the result of commercial experience and will not be covered in this paper. Some work was done, however, on means of increasing the useful life of retorts, which has been very profitable.

The retorts are maintained at an elevated temperature with a vacuum on the inside and atmospheric pressure on the

outside. This results in a considerable compressive stress on the retort walls. The retort ultimately fails by gradually collapsing under this long-continued compressive stress. Various means of improving this situation were considered and considerable experimental work was done on this problem.

The first idea was to restore the collapsed retort to its original shape by inflating with compressed air. It was found that with a standard retort at a temperature of 1150°C . compressed air at a pressure of 70 lb. per sq. in. would restore the retort to its original shape in a number of hours.

Retorts having an inside diameter of 10 in. and $1\frac{1}{8}$ -in. wall thickness collapse after an initial operating period of 60 to 90 days. After restoration to roundness with air pressure the life until the next collapse is 20 to 30 days. The procedure of restoring the retort to roundness is repeated every 20 to 30 days and the life is thus extended to an indefinite period. In our tests the life has been extended to eight months and the retorts are still in operation. During this period, the retorts collapsed a total of six times. This method of extending the life of the retorts has become standard commercial practice. Probably the best procedure is to apply air pressure at sufficiently short intervals to avoid very marked collapse of the retorts.

There is some evidence that a thinner walled retort when regularly restored to round by air pressure will give at least as long a life and at a lower cost.

Experiments were made with refractory liners placed inside the alloy retorts for the purpose of preventing collapse. The first trial was made with a $\frac{1}{8}$ -in. thick alloy sheath made from rolled sheet and welded. The welded joints failed in a few days. Two cast retorts having a $\frac{1}{2}$ -in. wall thickness and internal diameter of $11\frac{3}{4}$ in. were then obtained. These retorts were supported internally by a series of short silicon carbide tubes $11\frac{1}{2}$ in. outside diameter with $\frac{3}{4}$ -in.

wall. One retort was operated at a temperature of 1225°C . and failed, apparently because of some reaction with the silicon carbide. The second retort was put in operation at 1165°C . and is still in service after six weeks.

The silicon carbide liners prevented collapse and had no noticeable effect on magnesium production. Further work would be required to determine the most suitable refractory and the general practicability of the scheme.

The early reduction tests were made in iron retorts varying in wall thickness from $\frac{1}{2}$ to $1\frac{1}{8}$ in. The life of these retorts was very short because of rapid oxidation on the outside by the firing gases. Later the retorts were protected from oxidation by being placed inside a refractory sheath. Retorts protected in this manner gave a life of 3 to 4 months before oxidation caused failure. The strength of iron retorts at this high temperature compared favorably with that of alloy retorts and collapse of both retorts occurred in about the same period of time.

CONDENSATION

In this process the magnesium condenses in massive form on a steel sleeve inserted into the cold extension of the reduction retort. The main requirements found for good magnesium deposits are: (1) good vacuum; (2) freedom of the briquetted charge from volatile such as H_2O and CO_2 ; and (3) good separation of the alkali metals, sodium and potassium, which are contained in various amounts in the dolomite. In the early work of this investigation, difficulty was experienced with burning of the magnesium when vacuum was released at the end of a reduction cycle. This was caused by the magnesium being of a porous nature and containing sodium and potassium. The condenser during this period was water-cooled, which permitted condensation of the alkali metals.

A modified condenser was used later, which eliminated the water-cooling in the

condensing section. This condenser had a greater length and was designed to operate at a higher temperature. This permits condensation of the magnesium on the steel sleeve but the temperature is sufficiently high to prevent condensation of the alkali metals, which pass on to a separate collector and are removed independently of the magnesium.

CHARGING AND DISCHARGING THE RETORTS

This process involves batch charging and discharging of the retorts, which is a large labor consumer if performed manually. A scheme was developed whereby the briquets were charged into the retorts in a stream of high-velocity air through a small-diameter pipe. The wet-process briquets have sufficient strength to withstand this treatment but a considerable amount of breakage occurred with the weaker dry-process briquets.

A vacuum method of discharging the residue from the retorts was also tried. This involves the use of a stream of air eductor and works on the principle of a vacuum sweeper. The residue is removed through a small-diameter pipe inserted in the retort and is collected in a receiving tank placed between the eductor and pipe. This discharging device worked satisfactorily, and the time required to discharge a retort of 10-in. diameter, 5 ft. long, was less than one minute. The volume of air found necessary to carry the briquets through the pipe was about 180 cu. ft. per min. when a pipe 2 or 3 in. in diameter was used.

Insufficient work was done to develop either of these devices to the point of commercial use.

ACKNOWLEDGMENTS

Too many people contributed to this investigation to permit individual mention of more than a few. The authors wish particularly to express their gratitude to Mr. J. D. Sullivan, Chairman, Process

Research Division, War Metallurgy Committee, for his constant interest and support; to Mr. H. E. Bakken, Chairman of the Advisory Committee, and to the other members of the Committee,* who, both individually and as a committee, made numerous valuable suggestions; and to Messrs. E. C. Truesdale, H. C. Haupt, I. D. Wagner, M. D. Brewster, and C. M. McFarland, all of whom took important parts in the prosecution of the investigation.

DISCUSSION

R. LEPSOE.†—This paper gives an excellent account of the pertinent factors involved in the ferrosilicon reduction process of magnesium. The authors are to be congratulated for publishing it and disclosing the many interesting data.

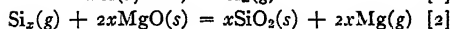
The paper shows the effect of time, temperature and grade of ferrosilicon on the so-called silicon efficiency, which is a practical term based on total silicon in ferrosilicon. Obviously, the efficiency or yield depends on the activity (silicon vapor pressure) of the silicon in the alloy. Several years ago I had the opportunity to study the effect of high temperatures, 1600° to 1800°C., on silicon-iron alloys containing 50 to 90 per cent Si, and noticed that invariably the final alloys had 30 to 35 per cent Si, indicating that there is at least one alloy, presumably of the formula FeSi, in which the activity of silicon as compared with the higher alloys is so small that its effect as a reducing agent is practically nil; viz., in an alloy containing 75 per cent Si and 25 per cent Fe, 12.5 per cent Si would be retained by the iron as unreactive FeSi, leaving 62.5 per cent "free" silicon. Or 100 per cent "reactivity" would correspond to maximum efficiency of $62.5/75 = 83$ per cent.

I have used Table 4 as a basis for a few calculations and find that as regards "reactivity" all the tests except 1 and 8 are in good agreement; viz., 83; 86; 87; 89; 85 and 83 per

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cent for 6 hr. at 1150°C. The percentages of "free" silicon in the total residue are as follows: 2.1; 1.6; 2.0; 2.9; 2.8; 2.8. Again tests 1 and 8 are exceptions (1.1 and 4.2 per cent). Similarly, the "reactivity" of aluminum (Table 7) varies between 85 to 90 per cent. These figures, together with others derived from Table 3, suggest first-order reactions as well as gas reactions, for example:



From equation given in International Critical Tables, the vapor pressure of solid silicon is 0.51 mm. at 1150°C. 1 mm. at 1219°C., and the heat of evaporation is 41,000 cal. The

increase in reactivity between temperatures 1150° and 1225°C. (Table 3) is

$$- \frac{4.6 \Delta \log k}{\Delta 1/T} = 19,000$$

i.e., about half the heat of evaporation of silicon. This suggests also that the silicon vapor within these temperatures is diatomic.

The practical significance of the foregoing suggestions tends to show that the silicon alloy for magnesium reduction should contain as little iron as possible. In my recollection it should, if properly organized, cost only a little more to make alloys containing 75 per cent Si and 15 to 20 per cent Al or Ca (balance Fe) than the ordinary 75 per cent Si, 25 per cent Fe grade.

The Melting and Refining of Magnesium

By C. E. NELSON,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE purpose of this discussion is to outline briefly the practices commonly followed in this country for the melting and refining of magnesium and its alloys. The processes used for the various forms of primary magnesium, as far as there are differences in the physical shape or behavior, will be discussed. The refining of general fine scrap or secondary magnesium was presented in an earlier paper.¹

Inasmuch as the use of fluxes is an essential part of all the melting and refining processes, the principal aim of this paper will be to deal with these in sufficient detail to point out their unique characteristics, in order to make their use more effective.

TYPES OF MELTING PRACTICE

All melting and refining processes for magnesium and its alloys require the use of fluxes. These fluxes have a magnesium chloride base and other halide salts or oxides are added to give a density or behavior exactly suited to the particular melting practice. The successful handling of magnesium depends upon the proper use of the correct fluxes.

There are four general methods of melting, summarized in the following paragraphs and treated in more detail in the section on Melting and Refining.

Open-pot Method

The open-pot method makes use of No. 230 flux.² The flux provides protection

during melting and a molten pool of flux into which the solid magnesium melts. It is stirred through the molten metal bath and agglomerates oxide or similar foreign bodies; then on quiet standing separates away, leaving the refined metal ball floating in an encircling layer of molten flux. It forms only a thin fluid film over the surface of the molten metal, which may be parted for hand-ladling processes and tends to cover the metal again after the ladle is removed. A very light dusting of the pot surface with fresh flux immediately after the ladle is removed is usually desirable.

The open-pot method is used generally in the following processes: (1) alloying and secondary smelting in the production of ingot, (2) in sand foundries for premelting and to a smaller extent for the production of small castings requiring hand ladling, (3) in permanent-mold founding for premelting and also direct ladling to castings, (4) for continuous methods of preparing metal in the production of billets or ingots from which wrought products are fabricated, (5) in general scrap recovery.

Crucible Process

The crucible process makes use of No. 310 flux, which has the property of being thinly fluid at the start, to provide protection and refining qualities, and then drying out or thickening after a time, leaving a protecting crust on the pot surface until the time of casting. At that time it can be readily skimmed off or held back, thus allowing the contents of the crucible to be poured out directly into castings without fear of flux contamination. This flux is not

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¹ References are at the end of the paper.

² All flux numbers refer to the designations of the Dow Chemical Co. See Table 1, page 395.

self-healing in its film protection, hence is not suitable for hand-ladling operations.

This method is used principally in the following processes: (1) sand and permanent-mold founding as a single-step melting, refining and pouring operation, or more commonly as a second step following the transfer to a casting crucible of molten metal from premelting units such as large open pots or tilting crucibles; (2) crucible processes in the batch method of melting, alloying, and pouring billets or ingots from which wrought products are fabricated; (3) the refining of die-casting scrap.

Reverberatory Process

The reverberatory process is a new development for melting magnesium. It has been stated by Beck^{2a} that hearth furnaces, whether gas or electrically heated, are unsuitable for the melting of magnesium alloys, owing to the large surface of the melt as well as to the contact between the gases and the metal or flux. Some confidence was obtained in the possibility of melting magnesium by direct radiation as a result of the successful experiments by the Dow company in melting magnesium in the resistor-heated type of Detroit electric rocking furnace. With this as a background, a reverberatory hearth furnace having a capacity of 1500 lb. of magnesium was built for experimental work. This unit was operated successfully using oil and gas as fuels.

Based on these preliminary experiments, a furnace with a capacity of approximately 12,000 to 20,000 lb. of magnesium was put into use. This furnace has operated for about two years and during that time six more similar furnaces have been placed in service.

Below the metal line these furnaces are lined with a refractory that is relatively nonreactive with the fluxes and the magnesium. The linings with the longest service record are of Tercod, a carbon-bonded

silicon carbide refractory having a carbon facing next to the metal bath. The walls and roof are of high-grade firebrick.

In operation, the solid charge is fed mechanically into one end of the furnace onto a preheating shelf, from which it is pushed into the bath by the introduction of the next charge. Metal is dipped or pumped out of a well at the opposite end of the furnace.

The consumption of flux for melting magnesium in these units has been the same as previously was required for standard open-pot operation. Similarly, the melting loss closely parallels that obtained in the more conventional methods of melting. Fuel efficiency is much better and would amount to about two thirds of that used in open-pot melting. Undoubtedly, the outstanding feature of the open-hearth operation is the very high melting capacity. The units in operation are capable of melting continuously at the rate of 4000 lb. of metal per hour.

Safety of operation is another notable feature, since the charging and preheating is all automatic and splatterings cannot reach the operators. Furthermore, the likelihood of a runout is remote, because the refractory construction is cold on the outside.

The field of use of the reverberatory is in large-scale continuous melting of magnesium or alloy ingot or heavy scrap. In such a process, it operates as a premelter for alloying or foundry operations. It is not considered suitable for the melting of fine magnesium or light scrap, because of the difficulty of applying adequate mechanical puddling and the development of the large amounts of sludge or dross that accompany the processing of these materials. Protection during melting and holding is provided by 230 or similar types of open-pot fluxes. In this method, the ultimate refining of the metal is largely obtained in the open-pot or crucible process that follows.

Die-casting Process

The die-casting process makes use of No. 220 flux, which gives no surface protection but is used only for refining the metal. Surface protection in this method comes from the use of a sulphur dioxide atmosphere, which is maintained in a closed dome over the pot. Only a very little flux is used as protection during melting down, and this is stirred through the metal thoroughly for refining. After a few moments of quiet standing, this flux, together with agglomerated oxides and dross, sinks to the bottom of the pot and is removed with the sludge.

TYPES OF MAGNESIUM

The two general types of primary magnesium that will be considered here are the well-known ingot made by electrolytic reduction processes and the crystalline condensed product from the newly introduced reduction processes such as the ferro-silicon-dolomite reaction.

Ingot

Little special description need be given to the magnesium ingot, since this product is a solid ingot that is already in a well-refined state through having been dipped from a fused salt or flux bath. The only significant impurity in this metal is iron, which normally is present to saturation (0.030 per cent iron) at the temperature of the electrolytic cell. The melting, alloying, and refining of this ingot presents no more difficulty than the routine melting of magnesium-alloy ingot.

Crystalline Magnesium

The melting and refining of the crystalline magnesium is somewhat difficult, and for this reason the following discussion will attempt to point out features in the proces-

sing of this material that are different from the standard practices discussed later.

Crystalline magnesium is finely divided and hence oxidizes readily. Furthermore, a variable and sometimes appreciable amount of oxide, nitrides, and other impurities are occluded with the crystals. Because of these, more care must be exercised during the melting of the crystals to use a fluxing technique that will not permit oxidation. Normally this is accomplished by charging the crystals into a "heel" of molten metal purposely left over from a previous batch, or into a bath of melted flux in the bottom of the pot. Liberal quantities of the same flux are dusted over the solid charge and as often as required to prevent the start of oxidation. The crystals are puddled into the metal or flux bath as rapidly as possible. After the charge has all melted down, more flux is added and stirred thoroughly through the bath, in order to separate out the oxide and dross inclusions. If the crystals are particularly clean and free from oxide and other undesirable materials, it may be sufficient to proceed with the normal alloying processes, followed by stirring of the fluxes through the bath and finally settling out of the dross and sludge and pouring of the refined alloy into ingots or castings.

If the crystals contain a large amount of oxide, or appreciable oxidation takes place during the melting, it is desirable to allow a few minutes quiet settling and then dip from the bottom of the pot as much of the dross and oxide as possible before proceeding to the alloying and refining steps. The decision as to whether the sludging out should be done before alloying, refining, and pouring would be made by the skilled operator, who can feel how much sludge is in the pot and knows from experience how much may be present and still permit proper refining and production of clean ingot. It has been noted that, for certain grades of crystals and scrap, refining may be facilitated by the addition to the 230

flux of certain agents such as fluorspar, or salts such as sodium or potassium chloride.

The magnesium crystals usually are relatively low in iron content but may contain sodium, potassium, calcium, and sometimes silicon as impurities. For all practical purposes, all except the silicon are

later stage wherever the production of high-purity alloys is warranted. For example, almost all the wrought magnesium alloys, except the Mg-Mn type, now in use in the United States are of high purity made possible by precipitation of the iron, which will be described later.

TABLE 1.—*Composition and Characteristics of Fluxes for Melting and Refining Magnesium, Dow Chemical Company*

Flux No.	Composition	Use	Amount of Flux Present in Pot during Operation, Per Cent	Approximate* Net Consumption of Flux, Per Cent	Characteristics and Remarks
220	57.0 KCl 28.0 CaCl ₂ 12.5 BaCl ₂ 2.5 CaF ₂	Die casting	0	1-3	A heavy bottom flux used for refining metal in a covered pot provided with SO ₂ surface protection. Flux is removed after refining. Used where dipping is so frequent that open-pot operation is impractical
230	55.0 KCl 34.0 MgCl ₂ 9.0 BaCl ₂ 2.0 CaF ₂	Sand and permanent mold casting Premelting Alloy production Scrap recovery Flux pots Alloying	10-20 5-10 10-20 10-20 100 0	4-6 2-4 3-6 4-15 <0.5	Characterized by high fluidity of surface film protection, allowing parting and recovering for ladling operations. High refining qualities. General open-pot flux
250	23.0 KCl 72.0 MnCl ₂ 2.5 BaCl ₂ 2.5 CaF ₂		0	Variable	Used for introducing manganese into alloys made by open-pot process with 230 flux. Reaction products approximate 230 flux behavior. Flux contains 31.7 per cent manganese by weight
310	20.0 KCl 50.0 MgCl ₂ 15.0 CaF ₂ 15.0 MgO	Sand and permanent-mold foundry Crucible alloying Die-cast scrap refining	1-3 2-5 2-5	3 2-5 2-5	Crucible-type flux characterized by being fluid at start for melting and refining, then drying out to crust that can be removed or held back for direct pouring
320	76.0 MnCl ₂ 13.0 CaF ₂ 11.0 MgO	Crucible alloying	0	Variable	Used for introducing manganese into alloys produced by the crucible process with 310 flux. Reaction products approximate 310 flux behavior. Flux contains 33.5 per cent manganese by weight.

* Based on weight of metal poured from a given operation.

removed by reaction with the flux in the melting and refining process. The iron content, on the other hand, will tend to increase up to the saturation value if this metal is melted, as is the common practice, in steel pots. The alloying metals normally added to commercial magnesium contain many times more impurities, such as iron, than are found even in the electrolytic magnesium, so that the natural purity of the crystals produced by the ferrosilicon process is lost unless special high-purity metals are used and the whole process is carried out in iron-free fluxes and melting equipment. In practice, therefore, it is more feasible to remove the impurities at the

The methods of handling distilled magnesium crystals are the same as those outlined briefly in the preceding paragraphs, except that normally it is not necessary to remove sludge before alloying and refining.

FLUXES AND CHARACTERISTICS

In order to give a clearer understanding of the types and uses of fluxes commonly employed for the melting and refining of magnesium, a list of compositions is included in Table 1.

The compositions and designations shown in this paper are those of The Dow

Chemical Co., but it should be pointed out that within the last year or two other suppliers have put fluxes on the market. Among these new suppliers are Basic Magnesium, Inc., and Permanente Metals Corporation.

EQUIPMENT FOR MELTING AND REFINING MAGNESIUM

No detailed information on equipment will be attempted here. The equipment most used may be indicated in the following outline:

1. *Open pots* may vary in capacity from 100 to 4000 lb. of magnesium. They are made of heavy cast steel. Particular care is taken to avoid the use of steels containing more than several tenths of a per cent of nickel, in order to prevent contamination of magnesium alloys melted therein. Cast-iron pots are brittle and often are too porous to hold the flux. They tend to grow in use, thus becoming still more porous; hence are not recommended.

2. *Crucibles* may vary in capacity from 20 to 2000 lb. of magnesium. The smaller sizes usually are made of welded steel and the very large sizes of cast steel. Ordinarily these are made with extra thick bottom sections to resist corrosion, and constructed so that this part can be readily replaced by cutting off the old section and welding on a new one. As with open pots, contamination by nickel in the steel must be avoided. Metallizing of these pots and crucibles with aluminum significantly increases their service life.

3. *Pouring ladles* should be constructed with a skimmer on the backside, for parting the flux, and a special bottom-pouringspout.

4. *Sludge ladles* are simply small hemispherical scoops ranging in size from 6 to 9 in. in diameter, depending on pot sizes.

5. A *skimmer* is a handy tool. It may be a flat, perforated plate about 6 to 9 in. in diameter, attached to a long handle.

6. *Sludge and flux pans* may be of ordi-

nary boiler-plate construction, made up in convenient sizes and shapes to permit easy removal of the frozen cake.

7. *Thermocouples* may be either Chromel-Alumel or iron-constantan and should be protected in the pots by a steel pipe or sheath.

8. Separate *flux pots* are essential to the production of high-quality magnesium-alloy ingots or castings using the open-pot ladling process. These pots usually are of the round-bottom cast-steel type having capacities of 400 to 600 lb. of magnesium. No. 230 flux is used to fill the pots, and all ladles, tools, and other utensils are washed periodically in this flux. This prevents undue splashing and agitation in the regular casting pot and prevents the carry-over of excessive oxide or other impurities into that pot, and thus into castings. Ladles should be kept smooth and clean at all times, as dirty ladles cause flux and oxide inclusions in the castings.

PREPARATION OF THE METAL FOR MELTING

Preparation of the metal is a very important part of any melting practice, since failure to clean the solid metal properly may lead to excessive gas or dirt in the melt and introduce harmful metallic impurities.

Aside from the regular precaution of preheating all metal that is to be charged directly into molten metal or flux, no particular precautions in preparation are necessary for virgin magnesium ingot or crystals.

Since heavy foundry scrap constitutes one of the largest sources of metal being melted, the following points will be of interest:

Oil or excessive moisture on the surface of the scrap is almost certain to lead to gas in the metal and excessive porosity in the product. These hazards are avoided usually by care in preventing oily materials

from coming into contact with the scrap and either predrying of the scrap in an oven, or sandblasting it just before melting.

Scrap should be remelted as soon as possible after the castings are sawed out, in order to prevent undue formation of hydroxide films on the surface.

Undesirable amounts of silicon may be introduced into the molten metal by improperly cleaned foundry scrap.

It is important that all material to be returned to the melting pot be thoroughly blasted and handled in such a way that no residual sand can be carried back to the melting operation.

If the metal becomes gassed, the remedy consists in long holding, with stirring, at low temperatures or, preferably, direct chlorine treatment.

MELTING AND REFINING PROCEDURES

The various types of melting practice are: open-pot melting and alloying, open-pot refining and pouring, crucible melting and pouring, two-step premelting and crucible melting, and die-cast melting.

Open-pot Melting and Alloying Practice

Ingot.—The largest proportion of all magnesium-alloy ingot used in the United States is produced by open-pot melting. The steps involved in converting magnesium into alloy ingot may be enumerated as follows:

1. A clean cast-steel open pot (usually between 600 and 4000-lb. capacity) is heated and a quantity of No. 230 flux approximately equivalent to 10 per cent of the weight of metal to be charged is melted therein.

2. Primary magnesium or heavy scrap of known composition, after thorough preheating on the edge of the pot, may be charged directly into this flux bath.

3. Additional No. 230 flux should be lightly dusted over the charge and pot surface.

4. The pot may be entirely filled with solid ingot, providing care is taken to dust thoroughly with the flux all parts of the charge. Any part of the charge that is added directly into molten metal or flux must be carefully preheated, in order to avoid danger of a blow and spattering when such material is added to the pot.

5. The pot should be watched diligently to make certain that no oxidation or burning takes place. Whenever required, a light dusting with flux will prevent oxidation.

6. While the charge is melting down, the required amount of alloying materials, such as aluminum, manganese or zinc, should be weighed out and placed on top of the solid charge, so that it will be preheated and gradually dropped into the pot as the supporting charge melts down.

7. As soon as all the materials are melted, additional quantities of fresh flux should be spread on the pot surface. If the manganese is added as No. 250 flux, it should be spread on the pot surface at this time and stirred into the melt. A vigorous stirring with a sludge ladle should be given from the bottom to the top of the pot, so as to produce a rolling action of the contents and to give uniform mixing of the batch. This stirring time would normally be from 5 to 10 min. This stirring also serves as a refining treatment to remove all oxides and dross from the metal and put them into the sludge.

8. At this point, a sample from the pot is taken for control analysis.

9. The batch is allowed to stand quietly for at least 10 min., or preferably longer, in order to give the flux and sludge a chance to separate completely from the ball of molten metal.

10. The metal is now in a refined state; and if the analysis is found to be satisfactory, the batch is ready for pouring.

11. Clean preheated ladles of the required sizes are used to dip the metal from the pot and pour into ingots. Since the ladle presumably has been cleaned in the

flux pot, it will be necessary to rinse off the excess flux by filling the ladle with metal several times and carefully pouring the metal back into the pot. After this procedure, the ladle may be used repeatedly to dip metal from the pot, until it shows oxidation or graininess, indicating that it is dirty and must be cleaned again in the flux pot.

It is very important that the operator carefully push back the flux film from a section of the pot surface before introducing the ladle. The ladle should be allowed to fill *slowly* over the back side. When full, it should be lifted through the parted section of the flux and a small amount of the metal poured back into the pot through the spout, so as to discharge any small amount of flux that may have been present in the spout. The ladle should then be raised from the pot and rested momentarily on the side of the pot, while the operator flicks a fine dust of flux over the surface, so as to prevent oxidation. This is a very important point from the standpoint of quality of the metal, and one most often neglected. Flux should *never* be placed on the pot just before the operator dips but should be applied immediately after the ladle is removed. In all dipping operations, care should be taken to avoid sudden and unnecessary motions in the pot, since these lead to mixing of the flux and metal.

12. Care must be taken in the pouring of the ingot to avoid turbulence of metal flow into the mold, as this leads to oxidation and poor quality of the ingot. The size of the ladle should be chosen to permit a small amount of metal to be left in the ladle after the ingot is full.

13. Protection for the ingot during pouring and solidification is provided by hoods over the molds and an atmosphere of SO_2 gas.

14. With reasonable care almost all of the metal in a given batch may be poured into ingots without risk of flux inclusions. In no case, however, should all of the

metal be ladled out into ingots, because of the likelihood of mixing the metal and sludge near the bottom of the pot. Usually it is more convenient to leave a certain small heel of metal in the pot (10 per cent), thus providing a pool of metal into which the next batch may be charged.

15. At this point, the thick sludge, composed principally of oxide, dross and flux, may be dipped from the bottom of the pot and the thinly fluid flux and metal proportion of the sludge be allowed to drain back from the dipper. The solid residue is placed in sludge pans. After this sludge is removed, the pot is ready for the next batch.

Scrap or Crystalline Magnesium.—As has been said before, the main deviations from the foregoing process in charging scrap metal or crystalline magnesium would be in the need for more careful protection against oxidation, more mechanical stirring to immerse the charge in the molten bath, and the possible addition of a sludging operation prior to the alloying and refining steps if it appeared advisable.

Open-pot Refining and Pouring Practice

Open-pot refining and pouring finds most use in the open-pot production of permanent-mold and sand castings. The steps involved for the two processes are so similar that they may be discussed together. The steps involved are as follows:

1. Cast-steel pots having capacities of from 600 to 1000 lb. magnesium are used. In starting a batch, the pot is first heated and a quantity of 230 flux, equivalent to about 10 per cent of the desired metal charge, is added.

2. When this flux is molten, preheated alloy ingot of the desired composition should be charged into the pot.

3. A fine dusting with 230 flux should be made over the charge and repeated as often as required during the meltdown, to prevent oxidation.

4. When the charge is entirely melted, a quantity of fresh flux should be added

to the pot. After this flux has melted, the entire contents of the pot should be stirred thoroughly to bring the flux into intimate contact with the molten metal. The metal temperature at this time should be preferably in the range of 1300° to 1350°F .

5. After this stirring and refining, the pot should stand quietly for at least 10 min. before any metal is dipped out.

6. The pot and contents should next be heated to about 1450° to 1500°F . and held at this temperature during the pouring cycle. Since the metal normally stands at this temperature for an appreciable length of time, a considerable grain-refining action is thus obtained.

7. Small sand castings may then be poured by ladling directly from this pot at about 1450°F . In permanent-mold casting, it is often necessary to pour at considerably lower temperatures; and for such cases the pot temperature would be dropped down to the appropriate level before pouring. The details of the ladling process would be the same as previously given.

In both sand and permanent-mold casting from an open pot, it is common practice to maintain a constant level in the pouring pot through the continuous addition, as required, of alloy ingot of the same batch or of hot casting scrap that came from the same melt. The large quantity of residual flux present in this type of operation seems to be adequate to refine this added metal separately. It should be pointed out that while there is about 10 per cent flux in the pot at any one time, sufficient flux is continuously carried along to reduce the overall flux consumption in the open-pot process to around 4 to 5 per cent. It will be necessary to dip the sludge from the bottom of the pot every 4 to 12 hr., depending on the rate of metal turnover.

Crucible Melting and Pouring Practice

Crucible melting is one of the methods commonly used for the production of sand

and permanent-mold castings. The steps in the process are as follows:

1. Steel crucibles in the size range of 60 to 550 lb. of magnesium are commonly used.

2. The crucible is placed in the setting, heated, and dusted with 310 flux.

3. Solid ingot of the correct composition and a portion of casting scrap are charged into the crucible.

4. No. 310 flux is carefully sprinkled over the entire charge.

5. After the charge is melted down and raised to a temperature of approximately 1350°F ., a quantity of fresh 310 flux (approximately 1.5 per cent) is added and allowed to melt, after which it is vigorously stirred through the metal. This refining operation should take about one minute and serves to agglomerate the dross so that part of it rises to the surface of the metal and the remainder goes to the bottom into the sludge.

6. The clinker-like dross that rises to the surface should be carefully skimmed off and fresh 310 flux immediately dusted behind the skimmer, to prevent reoxidation. If there is any question as to the quality of the refining treatment, a little more flux should be added, the stirring operation repeated and the melt again skimmed. The absence of substantial quantities of dross on the second skimming indicates that the refining treatment was adequate.

7. A moderate quantity (0.5 to 1 per cent) of 310 flux should then be spread over the surface of the crucible, the temperature raised to 1650° to 1700°F . and held for about 15 min. This treatment refines the grain in the alloy and causes the flux to "cure" or dry out, so that when the metal cools to the required casting temperature the flux either can be pushed back away from the lip or entirely skimmed off before pouring. Again sulphur, or a mixture of sulphur and boric acid, is used for protection during pouring. If the proper

refining and fluxing technique is not followed, the flux occasionally may dry out or crumble after superheating, thus allowing oxidation. It is a dangerous practice, as regards fluxing the castings, to add fresh flux at this stage. A very light dusting at the exact point of oxidation is permissible, but the general remedy is better refining and the use of more flux at the refining stage. It is quite important that no prolonged delay be allowed between the time the metal is at the superheating temperature—that is, 1600°F. or above—and the time of pouroff. The superheating treatment causes a desirable grain refinement, which is lost rapidly on standing at lower temperatures.

8. The crucible size should be selected for a given casting job, so that a small heel of metal will always be left in the crucible. After the pouroff is finished, the crucible is returned to the melting room and the sides spudded down, fresh flux being added when required to inhibit oxidation, and the dross and sludge skimmed out of the bottom of the crucible. The heel of flux and metal then remaining may be used as a starter for the next charge.

The normal consumption of 310 flux for this type of operation would be about 3 per cent.

Two-step Premelting and Crucible Practice

Two-step premelting and crucible melting is the most widely used method for the production of sand castings and is used to some extent for permanent-mold castings. In this type of operation, all of the ingot metal and foundry scrap is melted in large tilting crucibles, usually around 2000 lb. magnesium capacity. No. 230 flux is used for protection on this premelting crucible and the melting down operations are exactly the same as those described under open-pot melting practice. Ordinarily, the large premelting crucibles are operated on a batch basis, so as to provide a single large source of metal having the same

analysis. After this batch of metal has completely melted, it is refined and made of uniform composition by thorough stirring with No. 230 flux. Sludge must be removed from this crucible from time to time. Since the primary purpose of this unit is to melt the magnesium and provide some refining treatment, ordinarily the metal is not heated above about 1400°F. at this stage.

As often as metal is required for superheating and pouring, it is transferred from the premelters to smaller crucibles, usually of capacities between 60 and 550 lb. of magnesium, by tilting the large units. The metal in the latter crucibles is protected with No. 310 flux, which usually is dusted lightly into the hot crucible before the metal is transferred. These crucibles are then placed in settings and the metal temperature is raised to about 1350°F. At this point additional 310 flux (approximately 1.5 per cent) is added. As soon as this fresh flux is melted, it is stirred vigorously through the metal bath for a period of about one minute. This refining treatment brings a clinker-like dross to the surface and drops the rest of the impurities to the sludge. From this point forward, the process of superheating, pouring, etc., is the same as that previously discussed for the crucible melting and pouring practice.

In this type of operation, about 2 to 4 per cent of No. 230 flux would be used in the premelting and approximately 3 per cent of No. 310 flux in the crucible. This process offers many advantages, such as a double refining treatment and high-speed method of melting.

Die-cast Melting Practice

The die-cast melting method is used almost universally in this country for providing metal for die-casting operation. It is considerably different from any of the other practices in that it uses No. 220 flux, which has the characteristic of being able to refine the metal in the same way

as previously described fluxes but does not have the property of giving surface protection. Since the die-casting process requires the introduction of a ladle into the pot many times per minute, the use of a flux that gives surface protection would lead invariably to the inclusion of flux in the metal, because of the continued agitation. For this reason, this flux has been definitely designed to do the refining and then settle to the bottom, so that it may be completely removed from the pot with the sludge. Surface protection in this case is provided by an atmosphere of SO_2 , which usually is generated by burning sulphur in a hollow dome that operates as a cover for the melting pot. The ladle is introduced into the pot through a small opening through the cover. The SO_2 generated within the hollow dome is allowed to enter the space just above the metal in such a way as to blanket the molten metal surface and to retard the entry of air through the ladle opening. The primary meltdown in this case is done by dusting the surface of the pot with No. 220 flux and charging the solid metal into the pot, with careful attention and fluxing to prevent oxidation. When the batch is all molten, it is stirred thoroughly with the flux to agglomerate the oxide. It is next allowed to stand for about 10 min. to permit settling of the sludge and flux. The melt is then ready for sludging, which consists of removing the sludge with a skimmer perforated with $\frac{1}{4}$ -in. holes. The skimmer is preheated and put into the metal, scraping the bottom and sides of the pot.

When the skimmer is brought up with the metal and sludge, the molten metal runs out through the perforations, leaving only the sludge, which is dumped into a preheated pan. This process removes all of the flux and dross and the metal should now appear clean and shiny. It is advisable to allow about 10 min. quiet standing before beginning to dip metal from the pot.

The foregoing procedure is followed in starting up a new pot, but in normal operation it is preferable practice to keep the die-casting pot relatively full of metal. This may be accomplished by adding fresh ingot at a rate sufficient to maintain a constant metal level; or, still better, to do all of the melting in a separate premelting unit, using No. 230 flux and then transferring molten, refined metal directly to the casting pot by tilting or ladling from the premelter as convenient.

The usual range of pouring temperature for die casting is from 1175° to 1250°F. , so the oxidation tendency for the metal is relatively low. In this operation, the metal usually is protected by a thin film, which must be parted when the ladle is introduced. If there is evidence of undue oxidation on the metal surface after ladling, it means that the sulphur dome is not working properly. Sometimes a very slight dusting of sulphur or other similar agent may be required to control oxidation. In no case would fresh flux be added to the pot unless the entire refining and sludge-removal processes were to be repeated. In continuous operation, particularly if ingot is added directly to the pot, it may be necessary to re-flux the pot every 4 to 8 hr. Ordinarily from 1 to 3 per cent of No. 220 flux is used in the process.

Scrap.—The melting and refining of die-casting scrap presents a special problem different from that for the bulk of magnesium scrap, in that a certain proportion of carbonaceous materials, lubricants, etc., are present on the scrap, so that melting and refining in No. 230 flux as in ordinary practice is not satisfactory. A reddish scum, or film, of the carbonaceous material seems to stay suspended throughout the metal. This behavior is eliminated through the melting of such scrap in open pots or crucibles, using No. 310 flux instead of the usual 230. The No. 310 flux has the characteristics necessary to agglomerate

the carbonaceous film and refine this material. Melting procedures are similar to the open-pot operation with No. 230 flux for scrap recovery, except for the substitution of 310 flux.

DEVELOPMENT OF FLUX

The development of fluxes and the technique for their use in this country has gone a long way toward simplifying and improving the methods originally used in Germany and practiced abroad even at the present time. The original German practice made use of the naturally occurring double salt of magnesium and potassium chloride (carnallite). That this material is not exactly suited to flux practices was early recognized by the Germans and attempts were made to correct its behavior through the addition of other materials and more practically through the use of multistep flux operations.² In those processes, the molten metal is first washed with a thinly fluid flux, a second flux containing thickening agents is then added for the refining stages and finally a third flux containing thickening agents may be added, in order to absorb all the fluid flux and develop a crusting protection on the surface, which can be skimmed off or pushed back before pouring.³

Those who have been long associated with the development of magnesium in the United States will well remember the widespread difficulties with fluxed magnesium castings in the early days. These were caused primarily by the use of the carnallite fluxes. A definite development in this country has been in the evolution of a single flux such as No. 230, which, with reasonable use and appropriate technique, permits single-stage alloying or open-pot melting and pouring operations by providing a surface protection for the metal and permitting the flux film to be parted for ladling and then tending to re-cover this surface after the ladle has been removed.

The No. 230 flux has these characteristics as well as less tendency than other fluxes, to dry out or thicken during use, thereby providing a cleaner pot, better metal protection and better separation of flux from the metal. Another advantage has been that the amount of flux consumed for open-pot alloying operations has dropped from about 8 per cent down to 4 per cent.

What is probably a still more significant development is the No. 310 flux, which embodies in one agent all of the behavior and characteristics that are obtained by the multistep fluxing practice used abroad. More specifically, this flux at first is thinly fluid, so as to provide adequate protection during meltdown, and gradually thickens during the refining stages. While the metal is being superheated for grain refinement, the flux still provides protection and is converted during this high-temperature process to a surface crust, which may be skimmed off or parted for the pouring operation. Flux inclusions are never obtained in castings produced when this type of crucible flux is used correctly. It simplifies the foundry practice by requiring only one main flux and eliminates the guesswork of operators in using the correct proportions of the various fluxes required in the multistep operation. Similarly, it may be said that while better fluxes undoubtedly will still be discovered, the No. 230 and 310 fluxes provide a range of protection adequate to meet most melting problems.

It is also of possible interest to point out that the widespread use of premelting units in this country is a new and significant development in handling magnesium. The process is of interest primarily from the standpoint of facilitating production, in that a double refining treatment is not needed, as either 230 or 310 flux alone gives a sufficient refining action. More specifically, this permits an increase in melting rates and provides a large batch of metal of uniform and single analysis.

PRECIPITATION OF IRON

Iron is precipitated in the production of essentially all the wrought magnesium alloys except the Mg-Mn type used in this country. As previously stated, iron may occur in the original magnesium and is added in larger amounts in the aluminum and other alloying constituents, and may be picked up from the flux and from the pot itself. The iron is precipitated after the principal alloying materials have been added, usually by addition of manganese to a saturation value for a temperature above that at which the metal is to be poured. When manganese is present up to its solubility value, particularly in the presence of aluminum, iron is greatly reduced in solubility or tendency to stay in suspension, and is rapidly precipitated to the bottom of the pot. This concept is somewhat different from that pointed out by Beck^{2c} and others,⁴ in that they visualized an entrapment of the iron in primary crystals of manganese or silicon that could be used as the precipitation agents. In any case, the process operates consistently to produce iron contents on a commercial scale at an average of 0.001 per cent or less.

In actual practice, the manganese usually is introduced as manganese chloride, or, preferably, as No. 250 or No. 320 manganese flux. The former is used if the process is to be carried out in an open pot in the presence of 230 flux and the latter if it is to be carried out in a crucible in the presence of 310 flux. The manganese-flux compositions are balanced so that the reaction products are compatible with the respective fluxes.

While the iron-precipitation processes can be carried out successfully in steel pots or crucibles, any attempt to *remelt* or *reheat* high-purity alloys appreciably above 1300° to 1350°F. in contact with steel pots will lead to contamination by iron.

SUPERHEATING

Perhaps one of the most interesting

points in the behavior of magnesium and its alloys is the characteristic of a very marked grain-refining action obtained by means of a superheating treatment some 200° to 400°F. above its melting point. In this behavior, it is considered to be much like cast iron, and the theories and hypotheses used for the explanation of the behavior of the cast iron may be applied to magnesium with the substitution only of the alloy and the types of impurities.

Perhaps the most widely supported theory at the moment is that some material that at normal temperatures is too large in particle size to be effective is taken into solution at the high temperatures, and reprecipitates to form fine nuclei during the cooling process. The fact that after superheating the grain-refining effect deteriorates upon long standing at temperatures below the superheating range would lend credence to the idea that these nuclei are again coalescing and growing to their original form and relative ineffectiveness.

In any case, the superheating practice is very important in most casting operations, in that it provides finer grain size and a finer and more uniform distribution of the magnesium-aluminum compound, which further leads to more homogeneous heat-treated structures and high properties. The method by which the superheating effect is obtained has been discussed to some extent, and only a few more details will be mentioned here. Superheating effects may be obtained as low as 1500°F. but the time required at this temperature is rather long (several hours). As the temperature of superheating is raised to about 1700° to 1750°F., the time required to get the effect gradually drops off to approach zero.

It has been stated in the literature that the effect of superheating carries over through remelting steps.^{2d,5} This was found to be true to a limited extent, in that part of the time metal so treated might show the full benefits of superheating but more

often the effect would be only partially realized. In view of this action and the need for a good job of superheating prior to the actual pouring of the casting in production, in order to ensure uniformity of behavior, the advantage of using pre-superheated metal is considered questionable. To this point may be added the fact that in most casting operations the bulk of the material going back into the melting pots is foundry scrap, which already has gone through from one to five superheating operations in connection with previous castings and therefore would have whatever advantages are to be obtained through carry-over of superheating effects. A point on which we can fully rely is that if the *final* superheating before casting is properly done no additional benefits are realized from previous superheating.

SUMMARY

An attempt has been made in the foregoing pages to bring out the following significant points:

1. The use of the correct fluxes and the proper technique is fundamental in the melting and refining of magnesium.

2. Fluxes and techniques have been developed and are available for use in this country that are suited to the various types of melting and refining operations.

3. The use of a direct-flame reverberatory type of furnace is a new and demonstrated development for large-scale melting.

4. Magnesium alloys of controlled high purity are already being produced on a large commercial scale for wrought magnesium products and to a limited extent for castings. The use of magnesium of initial high purity is not a significant factor in this production, since impurities are added during alloying and melting. A precipitation method for lowering the iron after these operations appears most promising.

5. Superheating is very important in the production of high-quality castings. In actual practice carry-over effects of pre-superheating metal are not considered to

be sufficient to permit the elimination of a full superheating treatment just before pouring. Since 60 to 80 per cent of the charge being melted in foundry crucibles consists of foundry scrap that already has been repeatedly superheated, any benefits of such carry-over are already enjoyed. If the final superheating is proper, no additive effects are gained from previous superheating.

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DISCUSSION

F. A. Fox.*—It is hardly possible in a limited space to comment adequately on this interesting paper by Mr. Nelson. The methods he describes differ considerably from standard practice in this country. In our opinion the fluxing methods used by M.E.L. and the Elektron group possess important advantages over the methods described in this paper, in particular as regards simplicity of procedure, reduction in quantity of flux required, negligible risk of flux inclusions even with somewhat careless operation, and reduced metal losses. These methods are briefly outlined later.

Mr. Nelson's references to the original German practice and to "methods practiced abroad even at the present time" do not appear to be always correct and seem to us to be misleading. For instance, the impression might be gained, on reading Mr. Nelson's paper, that American melting and fluxing practice was ahead of that in the United Kingdom and that the development of fluxes Nos. 230 and 310 represented, in particular, an advancement over existing fluxes used elsewhere. Neither our own experience with No. 230 and No. 310 fluxes, nor the statements made by Mr. Nelson in his paper, appear to us to justify such a view. In fact, evidence pointing rather to the con-

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trary might be presented; for example, from the historical point of view, a flux essentially similar in behavior and purpose to No. 310 has been in use by one of our associates for about nine years. Further, the No. 310 flux itself is not unlike one of the German Elrasal fluxes in both behavior and composition.

The total consumption of fluxes in our own foundries in one complete operation involving melting, alloying, refining, superheating and casting of metal on the same scale as that of the Dow "open-pot alloying process" has for some years been 2.5 to 3 per cent of the weight of metal melted, whereas the Dow flux consumption in the "open-pot alloying process" alone is now 4 per cent.

The trouble with flux-contaminated magnesium castings in the early days of development of magnesium in America, mentioned by Mr. Nelson, and which appears to have continued long beyond "the early days," could hardly have been due primarily to the use of carnallite itself, because satisfactory castings were being prepared with similar flux materials in England, France and Germany at that time* when, incidentally, the tonnage of magnesium made and processed in Europe exceeded that in the U.S.A. by a ratio of about ten to one.

The "original German process" described by Mr. Nelson was probably never in use in three stages as standard melting practice. Even in 1936, a single, all-purpose, inspissated flux essentially similar to Dow 310, was supplied by I. G. Farbenindustrie A.G. to its casting licensees.

A detailed account of our fluxing process was recently published in *Magnesium Review and Abstracts* (Vol. 4, No. 1, Jan. 1944). For convenience, a brief outline of the methods used follows.

MELTING

Melting is carried out with a fluid flux Melrasal Z, corresponding roughly in behavior to Dow 230, which is sprinkled lightly over the ingots after the latter have been charged into the melting crucible, and subsequently applied as required to prevent burning. When the metal is molten, an inspissated flux, Melrasal E, which Dow 310 somewhat resembles, is used. This is stirred into the metal at

about 750°C. and a fresh layer is applied to the clean metal surface. Before pouring, the flux cover is gently drawn away from the lip of the pot and the metal is then cast.

An all-purpose flux, termed Melrasal UE, which is intended for melting, refining, and as a cover during superheating and casting, is suitable for ingot melts up to about 1000 lb. of metal.

No bath of fluid flux is used in melting, and at no time is it necessary either to scrape flux up through the metal from the bottom of the pot or to remove it from the metal surface. The total consumption of flux in a single operation involving melting, alloying, refining, superheating and pouring has already been quoted as 2.5 to 3 per cent of the weight of metal melted, and the gross metal loss is 2 to 3 per cent, of which a high percentage is recoverable by suitable treatment of the flux residue. Ladling processes for the transference of metal from one pot to another are avoided and die casting by ladles is considered undesirable.

OPEN MELTING AND ALLOYING PRACTICE

The use of highly fluid noninspissated fluxes in flux baths and for covering the metal seems to us most undesirable from the point of view of complete freedom of the castings from flux. The ladle casting process involving the use of a flux pot for washing the ladle, etc., appears to be a complicated, and, from the metal efficiency point of view, an uneconomic way of casting ingot. Ingot produced in this country is cast continuously from automatic, tilting 2-ton crucibles, into molds arranged on a continuous conveyor belt. An inspissated flux cover is used on the metal.

Melting in a flux bath is used by us only in the treatment of material obtained in the course of metal-recovery operations; this metal is cast into ingot and subsequently remelted.

CRUCIBLE MELTING AND POURING PRACTICE

The reason for some "clinker-like dross" rising to the metal surface and requiring removal is not clear.

In contrast with Mr. Nelson's warning against addition of fresh Dow 310 flux immediately before casting, the use of Melrasal E flux at this stage is perfectly permissible. If desired, the whole of the old superheated flux cover can be removed and a layer of fresh

* See, for example, French Air Ministry Report: *Le fusion industrielle des Magnésium et ses moulages en sable*, by A. Caillon (1938).

Melrasal E applied in its place; as soon as melting of the flux layer is complete it may be drawn back from the lip of the pot and pouring begun.

TWO-STEP PREMELTING AND CRUCIBLE PRACTICE

Apart from the additional stirring with No. 230 flux, the desirability of which is not appreciated, this process appears essentially to correspond with our standard practice.

DIE-CASTING PROCESS

In our opinion die casting should be done wherever possible from smoothly operating tilting pots using an inspissated flux cover. Where ladle casting is used we consider it preferable to cover the metal surface with Melrasal E, or, better still, with Melrasal UE, part the flux cover with a flux spoon or skimmer and then fill the ladle. A light dusting of Melrasal E is applied to the exposed metal surface in the pot when visible oxidation begins. Such a process may be conveniently combined with the dome filled with SO_2 described by Mr. Nelson, when it will be found that as development of thin oxide skin progresses, it is quite unnecessary to refine with Melrasal E, much less to sludge the pot; mere application of a fairly thick layer of Melrasal E to the metal surface followed by parting of the flux cover after melting is complete will enable casting to be resumed. This treatment of the metal surface with Melrasal E may be repeated at fairly frequent intervals, as required to maintain a clean metal surface in the pot.

MISCELLANEOUS

The comment that "flux inclusions are never obtained in castings produced when this type of crucible flux is used correctly" is no doubt justified, but it appears to imply that flux-contaminated castings may sometimes be produced when other types of flux or process are employed also "correctly." If so, what justification can there be for using such fluxes or processes at all?

The use of chlorine treatment mentioned by the author to degas melts of magnesium-base material is unknown in this country, as it is never necessary: a contributing factor here is probably the highly anhydrous character of our fluxes.

As for the grain-refining effect which the

author expects from the exposure of metal for appreciable periods to temperatures between 1450° and 1500°F (750° to 815°C .), we would not consider this an effective superheating or grain-refining temperature range, irrespective of the length of time involved.

For a few thin-section jobs it may be necessary to cast at temperatures as high as 1470°F . (800°C .): at these temperatures the unprotected metal burns vigorously, and sulphur is an inadequate protection. How would the author avoid in such a case contamination of the casting with oxide inclusions if the flux is "entirely skimmed off before pouring" (crucible melting and pouring practice)?

C. E. NELSON (author's reply).—As an opening statement pertinent to this discussion, the author would like to say that M.E.L. and Elektron fluxes and methods have been tested and compared with American fluxes and practices by the author and by other reliable foundry establishments in this country. This has been done recently as well as over a good many years. The conclusion has been that while in many cases the M.E.L. fluxes are the equivalent of those used in this country, there is no indication that they are superior in any respect.

There is no intention, either in this discussion or in the paper, to indicate that any classes of fluxes are not suitable for the purpose for which they were intended; rather, the theme is to point out that suitable fluxes are available, which, if applied and used correctly as indicated, will allow the production of castings that will meet the very high inspection standards in force in this country.

The terms "similar flux materials," "essentially similar," or "corresponding roughly to," used by Mr. Fox are not enlightening, since almost all the fluxes under consideration are made up from the same group of chemical compounds and differ only in respect to relative amounts present, depending on the intended use of the product. We know that small amounts of some of these elements markedly affect the behavior of the flux. We are very certain that castings made with carnallite would not regularly meet the inspection standards set up for castings in this country with respect to freedom from flux inclusions.

Melrasal Z, which is said to "correspond roughly in behavior to" Dow No. 230 flux, is

widely different in composition in that, for example, it contains a large proportion of CaCl_2 not found in the 230 flux and a very low relative proportion of potassium chloride. Actual measurements of the surface tension on these two fluxes show 230 to have a lower surface tension (90 compared to 104 dynes per cm.), which may account for the ease of repeated ladling from pots protected with 230 flux. Ladling from pot to pot is not practiced in this country.

The values given in the paper for flux consumption are for individual and single types of operation and the ranges, particularly on alloying, are made broad to cover all classes of magnesium melting such as crystals and a proportion of scrap. Wherever alloying, casting, superheating and pouring are carried out within one plant, or particularly in one continuous operation, figures on flux consumption agree with those quoted by Mr. Fox. Melting losses are also of the same order.

Regarding the removal of dross and sludge, it should be pointed out that most of the melting processes in this country are continuous or semicontinuous rather than batchwise. The "clinkerlike dross" is the same as referred to by E. F. Emley, in *Magnesium Review and Abstracts* (vol. IV, No. 1, p. 11) as "the thick layer of pasty metal oxide and flux," which he also states must be removed with the ladle before refining. This is not too common, especially in the two-stage crucible operation in connection with premelters. It may be due to the melting of dirty scrap direct in the casting crucible. This does not, however, offer any difficulty in production.

The Melrasal E flux is almost identical in both composition and behavior with Dow No. 310 but the author would definitely recommend that neither be used on the crucible just prior to pouring. These fluxes require time and temperature to inspissate and failure to allow for this is precarious.

We believe there may be confusion on the term "die casting," since the author refers to *pressure die casting* whereas Mr. Fox evidently refers to permanent mold casting. We would not favor either Dow 310 or Melrasal E fluxes for pot protection where a ladle must be introduced repeatedly at intervals of a minute or less and final castings are being poured. The

paper describes two workable methods to cover this type of operation; namely, the open pot with No. 230 flux or the SO_2 protected pot along with refining flux No. 220.

On the point of degassing and chlorine treatment of magnesium alloys, we would say that this is not common practice in this country and is considered only when scrap and ingot are not properly dried or handled or where there is abuse in the handling or exposure of the flux. The fluxes are all produced from anhydrous materials but take on water rapidly upon undue exposure in the melting rooms. This is equally true of the British fluxes. A few years ago we thought, like Mr. Fox, that there was no gas in magnesium alloys but experience in recent years has shown that it may be present and the resultant porosity takes the same form as the microshrinkage, and hence is difficult to distinguish from it. It is still true that if great vigilance is used, gas is not a serious problem on magnesium alloys.

No prolonged discussion will be given to the matter of low-temperature grain refinement. While, as stated in the paper, temperatures as high as 1650° to 1700°F. are necessary to get dependable grain refinement in a short time, we know from long production experience that metal held for 2 hr. or more at temperatures of 1450°F. or above will give dependable and effective grain refinement of the same order as obtained at the higher temperatures for short times.

In this country the inspissated flux cover may or may not be removed before pouring from crucibles. In either case adequate protection is provided by Dow No. 181 agent, which is much more effective than sulphur. Castings so produced are extremely clean and free from oxide.

One final point concerns Mr. Fox's comment that the three-stage fluxing system has never been used even in Germany. Within the last two or three years, M.E.L. interests in this country have advocated the use of a three-flux system consisting of Melrasal Z, E and FSF, to be used concurrently in that order. Our point has been that the use of too many different fluxes leads to mixed fluxes in the melting rooms and leaves too much to the judgment of nontechnical operators who must make the additions in such a way that one flux chemically balances or inspissates the other.

First Two Years Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant at Boulder City, Nevada

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(New York Meeting, February 1944)

THE present paper records a chapter in the history of the development of an electrolytic manganese industry in the United States.¹

A relatively large pilot plant at Boulder City, Nev., for the production of electrolytic manganese was conceived as part of the national defense program to make this country independent of foreign importation of manganese ore.

The first authorization, in November 1940, however, was for a plant of only several hundred pounds capacity. Improvements in process and subsequent additions to some sections authorized by subsequent appropriations have enabled the plant to produce as much as 2000 lb. of manganese a day for substantial periods of time.

Since in pilot-plant operation frequent changes are made in the flowsheet, the electrolytic manganese plant was constructed so that equipment could be rearranged with a minimum of expense and time. Several different kinds of the various types of equipment were installed for many

of the operations, so that the one most suitable for the process might be chosen.

Pilot-plant operations were begun in November 1941 and have been continuous except for brief shutdowns for installation of new equipment. More than one-half million pounds of manganese have been produced. The improvements in process, selection of equipment, and operational procedure developed are recorded here.

DEVELOPMENT OF THE PROCESS

The work of early investigators on the electrolysis of manganese solutions has been reviewed by Shelton.² Until the method of continuous production of manganese by electrolysis was perfected by Shelton²⁻⁴ and coworkers, no practical procedure had been devised. The method as originally developed by the Bureau of Mines will be described here only briefly.

The manganese dioxide ore was reduced in a rotating kiln-type furnace at 650°C. in an atmosphere of "city" gas. The calcine was leached with spent electrolyte and enough sulphuric acid to produce a neutral leach solution containing 25 grams manganese per liter as manganese sulphate and 200 grams per liter of ammonium sulphate.

Arsenic was removed from the solution by the addition of 0.05 gram iron per liter as ferrous sulphate followed by oxidation with manganese dioxide, and aeration, which precipitated the iron as ferric hydroxide. The solution, free from iron

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and arsenic, was treated with a mixture of 0.3 gram per liter of sodium ethyl xanthate and 0.2 gram per liter of potassium pentasol xanthate. After standing 6 hr., the nickel and cobalt had been precipitated by the xanthate and were removed by filtration. Sulphur dioxide was added to the solution to the extent of 0.1 gram per liter.

The purified solution was then electrolyzed in a lead-lined cell with the cathodes suspended in canvas-covered wooden frames, which formed diaphragms between the anodes and cathodes. The cathodes were of 10-gauge, 17 per cent chromium steel, and the anodes were $\frac{1}{4}$ in. corroding-grade lead.

During operations the manganese content of the catholyte feed was 24 to 25 grams per liter (pH, 7.2 to 7.6); the manganese content of the catholyte within the frame was 8 to 10 grams per liter (pH, 9.0 to 9.5); the manganese content of the anolyte was 3 to 6 grams per liter and the sulphuric acid content 25 to 30 grams per liter. The cathode current density was maintained between 18 and 20 amp. per sq. ft. About 20 per cent of the manganese fed to the cell was deposited at the anode as a hydrated manganese compound. An average current efficiency of 50 per cent was obtained over a 48-hr. deposition period. The metallic manganese deposited contained 0.20 to 0.30 per cent sulphur, which would make the metal undesirable for many purposes.

Dean¹ and coworkers improved the process with the aim of obtaining metallic manganese substantially free from sulphur. The purification step for the removal of cobalt and nickel was changed. It was found that the cobalt and nickel could be precipitated from solution by the addition of sulphide ion as barium or ammonium sulphides. Electrolytic manganese produced from solutions purified by sulphide contained little or no sulphur.

Preliminary tests also indicated that the leach solution could be purified by the

addition of powdered metallic manganese, which precipitated the impurities. Although this method of purification showed promise, it has not been demonstrated on a large scale.

The results of the work of the early Bureau of Mines investigators was sufficiently encouraging to justify construction of a commercial plant at Knoxville, Tenn., by the Electro Manganese Corporation,⁵ which has been operating a 2-ton plant successfully since 1938. The plant capacity was increased to 4 tons per day in early 1943. This plant is using the basic process as developed by the Bureau of Mines in 1936-1938.

Construction of the Boulder City pilot plant was begun in April 1941. While the pilot plant was under construction, extensive laboratory investigations were carried on and the work reported by Woodman and Jacobs;⁶ it will be briefly reviewed here.

Results of small-scale experiments showed that the reduction of manganese ores could be accomplished with coal, coke, natural gas, butane or oil. Although the reduction could be most easily controlled and carried out using oil or a reducing gas, the geographical location of a plant would determine which of the five reducing agents would be most satisfactory from the economic standpoint.

The calcine was leached in small lead-lined wooden tanks to a pH of 2.0 for $1\frac{1}{2}$ hr.; then the solution was neutralized to a pH of 6.0 with calcine. An extraction of 90 per cent of the manganese was obtained. The raw solution was decanted from the leached tails and the solution purified by the addition of 0.4 gram of hydrogen sulphide per liter of solution. All of the metallic impurities were precipitated as sulphides and were removed by filtration on a plate and frame filter press. This filtrate is theoretically pure but does contain colloidal sulphur and colloidal metallic sulphides and organic matter from the

ammonium sulphate. It was found that if 0.1 gram of iron per liter of solution was added as copperas and the solution was oxidized with air and filtered, all of the aforementioned materials were removed. This was an important improvement, because it always ensured a pure solution for electrolysis.

In the early Bureau of Mines process, the cathodes in the electrolytic cell were suspended in diaphragm-covered compartments. A normal operating cell contained 28 anodes and 27 cathodes. This design was necessary because of the manganese oxides formed at the anodes, but this cell had many undesirable features because each cathode compartment had to be fed separately; consequently, manganese was being plated from 27 different catholytes. This involved careful control of pH and solution content. As the quantity of catholyte was so small, it was difficult to prevent the pH from becoming too high, with consequent precipitation of manganese hydroxide. Also, the cells could not be operated at a current density above 30 to 35 amp. per sq. ft., because the pH would become too high, causing the manganese to precipitate.

It was decided that these difficulties could be overcome by placing the anodes inside the diaphragm compartments. However, before this could be done, it was necessary to have an anode at which little or no manganese oxides would be precipitated. A lead-tin-cobalt alloy was reported by Fink⁷ to prevent the formation of manganese oxides, but an anode of this alloy is difficult to make and has a rather short life. A perforated lead-silver anode was developed, which reduced the amount of manganese precipitated at the anode from 25 per cent for pure lead to 1.0 per cent.

The use of lead-silver anodes made possible a design wherein the anodes were inside the diaphragm compartments and all the cathodes were plating from the

same catholyte. This simplified cell control and allowed the electrodeposition to be carried out at cathode-current densities as high as 70 amp. per sq. foot.

The optimum conditions for the electro-winning of manganese were given by Woodman and Jacobs as follows:

Purified feed solution.....	40 to 50 grams per liter Mn as $MnSO_4$ 125 to 150 grams per liter ammonium sulphate 0.10 grams per liter sulphur dioxide 8 to 16 mg. per liter glue
Anolyte.....	10-20 grams per liter Mn as $MnSO_4$ 25 to 40 grams per liter sulphuric acid 125 to 150 grams per liter ammonium sulphate
Current density...	40 to 60 amp. per sq. foot
Catholyte pH.....	6.0 to 7.2
Anodes.....	Pb and 1 per cent Ag inside diaphragm
Cathodes.....	$\frac{3}{16}$ -in. aluminum treated with aluminum powder
Diaphragms.....	canvas or micropore rubber
Voltage.....	4.8 to 5.4
Kw-hr. per lb. Mn.	3.6 to 3.9
Current efficiency..	60 to 65 per cent

THE PILOT PLANT

All of the pilot-plant buildings are of steel construction covered with corrugated, galvanized-iron sheeting. The crushing plant is in a separate small building. Roasting, leaching and purification equipment is installed in the hydrometallurgical building, with all storage tanks and thickeners in the open. The cell room and generator are in a separate building. The flowsheet of the plant is shown in Fig. 1.

Ore is delivered to the crushing plant by trucks into a wooden bin through a grizzly. Oversize ore is broken through the grizzly by hand. Crushing is accomplished by a jaw crusher and rolls in closed circuit with a vibrating screen. An inclined belt con-

veyor delivers the crushed ore to the hydrometallurgical building, where a Jeffrey vibrating conveyor distributes it to any of ten 5-ton steel storage bins. From

of the ore; one is a 5-ft., 10-hearth Skinner furnace with muffled hearths, so that it is indirectly fired, and the other is a Traylor multitube rotary kiln consisting of five

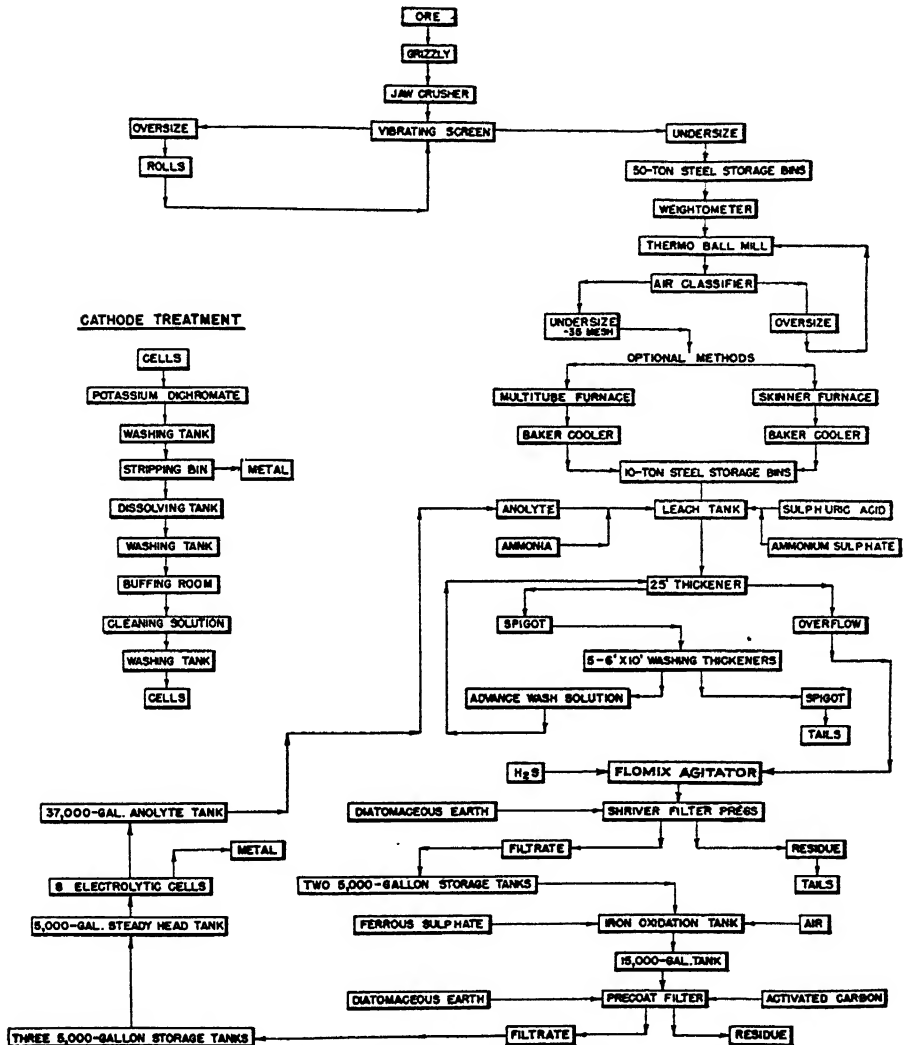


FIG. 1.—FLOWSHEET OF ELECTROLYTIC MANGANESE PILOT PLANT.

the storage bins, the ore is weighed in buggies and fed to a Hardinge thermal ball mill equipped with an air classifier, where it is ground dry to -35-mesh.

Two furnaces are available for reduction

10-in. alloy-steel tubes inside a brick-lined shell. Ore travels through the tubes and the fire is on the outside of the tubes. Each furnace discharges into a Baker cooler, where the calcine is cooled to below 100°C.

before entering the atmosphere. This is necessary to prevent reoxidation of the reduced ore. Both furnaces are fired with oil, and the roasting is carried out at 700° to 750°C. Reduction is accomplished by dropping oil on the ore as it enters the multitube furnace. Calcine discharges from the coolers into ore buggies and is transported to a 10-ton steel bin or directly to the leaching tanks. Since manganous oxide reoxidizes rapidly in air, it is not stored more than 24 hours.

Leaching is done in 3500-gal. batches in two 8 by 10-ft. brick-lined steel tanks equipped with stainless-steel propeller-type agitators. Spent electrolyte from the cells, containing 8 to 10 grams per liter manganese as manganese sulphate, 135 to 140 grams per liter ammonium sulphate and 43 to 50 grams per liter sulphuric acid, is drawn into a leach tank. Reduced ore is then added and leached for 1 hr., or until the pH has risen to 3.0. Sulphuric acid and ammonium sulphate are added as needed, so that the finished leach contains 32 to 36 grams manganese and 135 to 140 grams ammonium sulphate per liter. After the desired pH and manganese concentration have been reached, the leach is neutralized by the addition of ammonia gas. The resultant neutral solution is pumped to a 25-ft., acidproof steel thickener. Spigot discharge from the thickener containing barren tails, ferric hydroxide and aluminum hydroxide is washed countercurrently in five 10-ft. acidproof steel thickeners. After being washed free of manganese and ammonium sulphate, the residue is pumped to a tailing pond. Oliver diaphragm slurry pumps are used on all the thickeners and for discharging the leach tanks.

In addition to manganese and ammonium sulphate, the neutral leach solution, which overflows from the 25-ft. thickeners, contains small amounts of iron, arsenic, copper, zinc, lead, nickel, cobalt and molybdenum. All these impurities must be removed before electrolysis.

As the first step in purification of the solution, it flows by gravity from the neutral thickener overflow storage tank through a Nettco Flomix, where hydrogen sulphide gas is added. The Flomix is a small, stainless-steel, totally enclosed agitator flanged to fit a 3-in. line. The solutions are vigorously agitated by the Flomix, and complete precipitation of the impurities as sulphides results. After the solution leaves the Flomix, it is pumped directly to a Shriver plate-and-frame filter press, where the precipitated sulphides are removed from the solution.

Although the solution is now free of metallic impurities, it contains colloidal sulphur, colloidal metallic sulphides and organic matter that is introduced with the ammonium sulphate. These materials are removed by adding copperas and oxidizing the iron with air. The iron precipitates as ferric hydroxide; this precipitate absorbs the sulphur and colloids and also removes any residual arsenic and molybdenum that were not precipitated by hydrogen sulphide. An Oliver precoat filter is used to filter the iron hydroxide from the solution. A mixture of diatomaceous earth and activated carbon is used as the filter precoat. The resultant solution is now pure and ready for electrolysis. It is stored in four 10 by 10-ft. acidproof steel tanks, to be drawn into the cell room as needed.

In the cell room, electrolysis is carried out in eight lead-lined wooden tanks, 9.5 by 2.5 by 3.5 ft. inside dimensions and connected in series by a 2 by 7-in. copper busbar suspended on the side of the cells. Each tank has a capacity of 28 anodes and 27 cathodes, spaced $3\frac{1}{2}$ in. from anode to anode, and is supported by glass blocks on concrete piers. The cathodes are held in place on their busbar by cadmium-plated copper clips, and the anodes are bolted directly to the bar. Power is furnished by a 450-kw. twin motor-generator set driven by a 700-hp. synchronous motor. Purified solution containing 34 to 36 grams per liter

manganese as manganese sulphate, 135 to 140 grams per liter ammonium sulphate and 0.1 gram per liter sulphur dioxide flows to the cells through a 2-in. lead line on the

the diaphragms in a common anolyte. It was found to be advantageous to reverse the position of the anodes and cathodes, for reasons that will be discussed later; there-

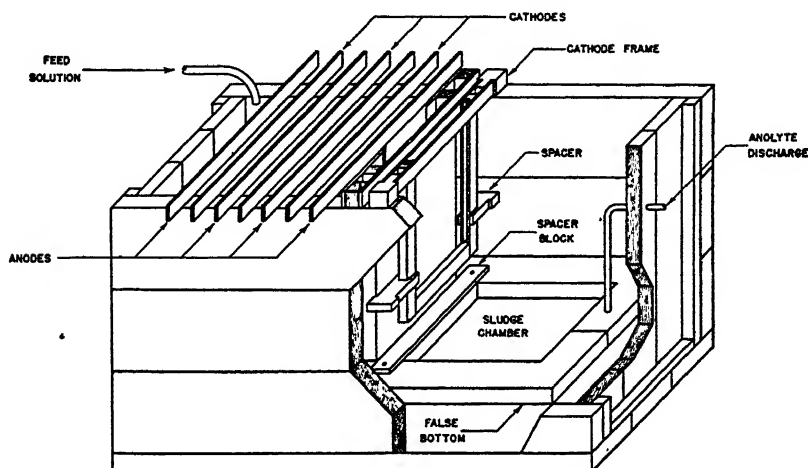


FIG. 2.—CELL USED IN PILOT PLANT FOR MAKING ELECTROLYTIC MANGANESE.

side of the tanks. Flow rate is controlled by rubber-lined diaphragm valves at each cell. Sulphur dioxide is added to the solution in the main line as it enters the cell room, to prevent precipitation of manganese hydroxide.

The cathodes are type 316 stainless steel, 18 by 36 by 16-in. gauge. Two copper strips $\frac{3}{8}$ by $1\frac{1}{2}$ in., covered with lead, are brazed along the top of the cathode to carry the current. A semimirror finish is maintained on the cathode by buffing every fourth day. The anodes, 15 by 32 by $\frac{1}{4}$ in., composed of 99 per cent lead, 1 per cent silver, are cast and drilled with $1\frac{3}{8}$ -in. holes so that 40 per cent of the area is void. This is necessary to increase the anode-current density, which minimizes the formation of manganese oxides.

As manganese cannot be electrodeposited efficiently from acid solution, the anolyte and catholyte must be separated by a diaphragm. In the original process, each cathode was in a separate canvas-covered frame, which necessitated a separate feed line to each. The anodes were outside of

fore the cell now used in the pilot plant has the anodes placed inside canvas-covered wooden frames, which are open at the bottom. The cell has a false bottom 10 in. above the main bottom, in which a rectangular area the width of the anode frames is cut out. This false bottom is completed by the anode frames and wooden spacer blocks, which fit between the anode frames, ensuring proper spacing. In this manner, a lower compartment is formed in the cell, into which the oxide at the anode falls. Phenolic resin frames hold the cathodes in place in the cell (Fig. 2).

Solution flows through the cells as follows: The purified solution entering the catholyte from the feed line along the side of the cell flows through the canvas diaphragm into the anolyte compartment, down into the lower compartment formed by the false bottom, and is then discharged from the cell through a 2-in. lead pipe rising from the false bottom at one end of the cell and out through the side at the desired height. A lead-lined wood launder conveys the spent electrolyte to a tank in

the basement, where it is pumped to the leaching plant for leaching more reduced ore.

The electrolyte in the cells is cooled by circulating cold water through lead coils in the cells. The water is cooled in the summer by an ammonia compressor and by an evaporative cooler in the winter.

Cells must be broken down at the end of 6 to 8 weeks for cleaning and replacement of diaphragms. Calcium sulphate crystals form on the anolyte side of the canvas diaphragm, reducing the porosity to the point where the solution will not flow through it.

Electrodeposition conditions are as follows:

Anode.....	99 per cent Pb, 1 Ag. 15 by 32 by $\frac{1}{4}$ in. 40 per cent void 28 anodes per cell
Cathode.....	Type 316 stainless steel 18 by 36 by 16-in. gauge 27 cathodes per cell
Current density.	Anode: 81 to 90 amp. per sq. ft. Cathode: 45 to 50 amp. per sq. ft.
Cell voltage....	5.0-5.3
Feed solution...	Mn: 34 to 36 grams per liter (NH ₄) ₂ SO ₄ : 135 to 140 grams per liter SO ₂ : 0.15 gram per liter
Catholyte.....	Mn: 8 to 10 grams per liter (NH ₄) ₂ SO ₄ : 155 grams per liter (calculated from ammonia content) SO ₂ : 0.10 gram per liter
Anolyte.....	Mn: 8 to 10 grams per liter (NH ₄) ₂ SO ₄ : 135 to 140 grams per liter H ₂ SO ₄ : 43 to 50 grams per liter
Diaphragm.....	18-oz. canvas
Duration of electrolysis.....	24 hr.
Pounds Mn per cathode.....	10 to 12
Current efficiency.....	60 to 65 per cent

After deposition for 24 hr., the cathodes are removed from the cells and dipped in a 1 per cent solution of potassium or sodium

dichromate, to prevent oxidation of the manganese. They are then washed in a spray tank and air-dried. The deposited manganese is stripped from the cathode by flexing and striking with a rubber mallet, with a recovery of 98.5 to 99.5 per cent of the metal. The small quantity remaining on the cathode is dissolved in a tank containing spent electrolyte from the cells. After the residual manganese is removed, the plates are washed in a spray tank. Every fourth day the cathodes are buffed and then cleaned with a standard alkaline soap cleaner. After being washed free of cleaner, they are ready for the cells.

Pilot-plant operations have been continuous, with few exceptions, and the effect of the variables of the process has been studied. As many of the factors in the process can be varied over wide ranges, it was frequently necessary deliberately to operate the plant under conditions that were not conducive to efficient operation, to obtain the required data.

A research laboratory was maintained in conjunction with the pilot plant at all times, and the work of both was closely coordinated. The results reported here were obtained in small laboratory equipment and in the large plant equipment. Where the results of the two were relatively concordant, no distinction will be made, but where large variations were encountered it will be so noted.

Although the pilot plant was operated primarily for the purpose of obtaining data, more than 550,000 lb. of metallic manganese was produced during the first 2 years of operation.

ORE

The ore used in the pilot-plant work is from the Three Kids mine, Las Vegas Wash, near Lake Mead, Clark County, Nev. It was chosen because of its availability and the fact that it is similar to ore from many other deposits in the country. The manganese is present as the dioxide,

and the ore is an earthy material or wad, with which are intermixed small quantities of psilomelane and manganite. Minor amounts of quartz, mica, gypsum, decomposed tuff, and opal and minor amounts of undetermined silicates make up the non-metallic portion of the ore. It is a light, porous, amorphous-appearing mass that breaks down to granular particles and slimes on wetting. Because of its extreme porosity, it can be reduced and acid-leached without fine grinding.

Both high-grade and low-grade ores were used. Typical analyses are shown in Table 1.

TABLE 1.—*Analysis of Three Kids Ore*
PER CENT

Constituent	High-grade Ore	Low-grade Ore
Mn.....	38.5	25.0
SiO ₂	14.0	27.5
CaO.....	1.68	2.63
MgO.....	2.22	0.37
Fe.....	0.70	1.31
Cu.....	0.0004	0.35
Ni.....	< 0.002	< 0.005
As.....	0.02	0.05
Pb.....	1.66	1.87
Al ₂ O ₃	2.24	
S.....	0.51	0.64
Mo.....	0.02	

Although the Three Kids ore is the only one that has been used in the pilot plant, electrolytic manganese has been made successfully in the laboratory from several others, including low-grade oxide ores and carbonate ores. As it is necessary always to electrolyze from a pure solution, the only problem involved in changing from one ore to another is modification of the purification scheme, to ensure complete removal of all undesirable impurities.

CRUSHING AND GRINDING *

The ore is crushed through ½ in. by a jaw crusher and rolls and then ground to 95 per cent through 35-mesh in a 5 by 2-ft. Hardinge ball mill equipped with an air classifier. Preheated air entering the classifier dries the ground ore and removes it

from the ball mill. Ore is fed to the mill by a Jeffrey vibrator at the rate of 1 ton per hour. A cyclone collects the ground product and drops it in a steel storage bin. A ball load of 3200 to 3600 lb. is maintained in the mill.

TABLE 2.—*Screen Analysis of Three Kids Ore*
PER CENT RETAINED ON SCREEN

Mesh	Ball-mill Product	Calcine	Leach Tails
35	3.37	1.13	0.69
48	2.86	1.02	1.04
65	6.50	3.18	1.56
100	11.29	14.09	0.52
150	37.43	20.16	8.52
200	20.91	31.27	6.78
-200	17.74	29.15	80.89

A typical screen analysis of the ground ore is shown in Table 2. Since the Three Kids ore is very porous, it need not be ground finer than 8-mesh to obtain complete reduction and leaching, but since the leach tails cannot be readily handled in the pumps available and in the thickeners, the ore is ground to 95 per cent minus 35-mesh. Dust losses from the crushing and grinding are rather high, usually 4 to 6 per cent, but these could be reduced markedly by a baghouse.

ROASTING

The manganese dioxide in the ore must be reduced to manganous oxide to make it soluble in sulphuric acid. Roasting has been accomplished in the Traylor multitube and Skinner furnaces but since the multitube is the smaller and more nearly produces the requirements of the pilot plant, the Skinner furnace was used only for short periods of time, to obtain special data. The attrition during roasting is sufficient to grind the ore considerably, as shown in Table 2.

Skinner Furnace

The Skinner furnace used is a modified-type multiple-hearth furnace with 10

interior hearths and a drying hearth on top, which is open to the atmosphere. Muffles are attached to the underside of hearths 5, 6, 7, and 8; therefore, heating on hearths 6, 7, 8 and 9 occurs by radiation from the Carbofrax muffle floors. The hot gases from muffles 4, 5, 6 and 7 pass through connecting flues to a main vertical flue, where they may be discharged to the atmosphere though a separate stack or pass through damper-regulated connecting flues to any one of hearths 1 to 4, thereby furnishing heat to the raw ore on these hearths.

The central shaft, made of heat-resistant alloy, is covered with insulation from the tenth hearth to the underside of the arms of No. 1 hearth. It has four arm sockets for each roasting hearth and six arm sockets for the drier hearth. Hearths 1 to 6, inclusive, have four Meehanite metal arms each, with the necessary rabble teeth, and hearths 7 to 10, inclusive, have two arms each of Fahralloy. The hollow central shaft and rabble arms may be cooled by air supplied from a low-pressure fan, and the resultant hot air passes out through a short stack attached to the top of the shaft.

Fuel oil No. 3 was used for both heating and reduction. The quantity of oil required for each was measured separately but, since the reduction oil also furnished heat, the separate quantities are not completely accurate. Regardless of the tonnage of ore roasted, the ratio of 45 per cent of the total oil consumption for heating and 55 per cent for reduction held relatively constant. The reducing oil was dropped on the ninth hearth.

Furnace temperatures during a typical run are shown in Table 3. It was found

TABLE 3.—Average Temperatures in Skinner Furnace

HEARTH	TEMPERATURE, DEG. C.
3, 4, 5.....	250
7.....	675
8.....	675-750
9.....	675-700
Flue gases into 4.....	550
Stack outlet of furnace.....	200

that 700°C. was the minimum reducing-zone temperature for efficient reduction. The most efficient tonnage rate was 22 tons per day. A leach extraction of 95 to 98 per cent of the manganese was maintained under the above conditions. The results of a typical run are shown in Table 4.

TABLE 4.—Reduction of Manganese Ore in Skinner Furnace

Wet feed, lb.....	280,573
Water, per cent.....	9.9
Dry feed, lb.....	252,744
Mn in feed, per cent.....	24.57
Calcine produced, lb.....	218,415
Mn in calcine, per cent.....	27.41
Oil consumed, gal.....	2,108
CO in stack gas, per cent.....	1.0
Oil per ton dry feed.....	16.2

Traylor Multitube Rotary Kiln

The multitube kiln has a maximum daily capacity of 6 tons of calcine. It is a brick-lined steel shell 25 ft. long containing five 10-in. alloy-steel tubes equidistant from one another. Ore is fed to the tubes by a screw conveyor and the kiln is fired with oil in a brick firebox. The fire is around the tubes, thereby heating the ore indirectly. A Baker cooler is connected to the discharge end of the kiln so that the calcine is cooled to below 100°C. before it is discharged into the atmosphere. The kiln must be operated with very little draft on the tubes, to prevent air from being drawn in around the packing and the cooler discharge. The combustion gases are recirculated to the firebox. Oil is dropped on the ore in the screw feeder, and the rate is controlled so that the CO content of the reduction gases at the stack exit is 1.0 to 1.5 per cent. A calcine from which 95 to 98 per cent of the manganese can be leached is readily obtained under proper conditions.

Tables 4 and 5 show that the oil consumption per ton of feed in the multitube furnace is much higher than in the Skinner furnace, because the multitube is not as efficient thermally, owing to high radiation losses, and because the reducing gases in the Skinner flow countercurrent to the ore whereas in the multitube the gases from

the reduction are drawn off at the discharge end of the furnace. An attempt was made to operate the multitube with countercurrent flow of the reducing gas but because of the arrangement of the five tubes it could not be done successfully.

TABLE 5.—*Reduction Roasting in Multitube Rotary Kiln*

Wet feed, lb.....	96,174
Mn in feed, per cent.....	32.53
Dry feed, lb.....	92,876
Water in feed, per cent.....	3.43
Calcine, lb.....	82,341
Mn in calcine, per cent.....	37.90
Reducing oil (No. 200), gal. per ton dry feed.....	14.75
Heating oil (No. 200), gal. per ton dry feed.....	36.21
Temperature in hot zone.....	750°C.
Temperature of combustion gas at stack exit.....	275°C.
Temperature of reducing gas at stack exit.....	175°C.

LEACHING

After the manganese ore has been reduced, it is leached with spent electrolyte, containing sulphuric acid, from the cell room. Spent electrolyte is drawn into the brick-lined leach tank and calcine is added over a 30-min. period. The final volume of the leach is 3400 to 3600 gal. Vigorous agitation is furnished by a stainless-steel ship-type agitator. After the calcine has been charged, sulphuric acid is added to keep the pH at 2.5, which is the finishing point of the leach. Ammonium sulphate also is added at this point as needed to maintain a concentration of 135 to 140 grams per liter in the finished leach solution. A temperature rise of 12° to 16°C. occurs during leaching, and the total time required for leaching is 1¼ to 1½ hr. A manganese extraction of 98 to 99 per cent is obtained. There is considerable sliming of the ore during leaching, as shown in Table 2. Table 6 shows the solution concentrations before and after the leaching. Since the leach residue must be washed thoroughly to remove manganese sulphate and ammonium sulphate, it is necessary to allow for dilution by the wash waters in arriving at the final manganese and ammonium sulphate concentrations.

After the leach is finished at a pH of 2.5, it must be neutralized to a pH of 6.5. This can be done by ammonia or by adding cal-

TABLE 6.—*Solution Concentrations during Leaching*

GRAMS PER LITER

Constituent	Spent Electrolyte	Leach Solution at pH 2.5	Leach Solution at pH 6.5	Leach Solution after Residue is Washed
Mn.....	10.5	37.5	36.5	34.7
(NH ₄) ₂ SO ₄	136.2	137.8	144.6	137.6
Fe.....	0.0015	0.16	0.001	0.001
As.....	0.0005	0.02	0.0018	0.0017
Ni.....	<0.001	<0.001	<0.001	<0.001
Co.....	<0.001	<0.001	<0.001	<0.001
Cu.....	0.006	0.04	0.01	0.0095
SiO ₂	0.02	1.29	0.02	0.0285
MgO.....	11.8	12.4	12.4	11.8
CaO.....	1.20	1.25	1.25	1.20
Al ₂ O ₃	0.01	0.29	0.01	0.01
Mo.....	0.0007	0.008	0.005	0.0048

cine. If calcine is used as the neutralizing agent, the over-all leach extraction is lowered from 98 to 99 per cent to 92 to 95 per cent. If ammonia is used, the higher leach extraction is obtained and the amount of ammonium sulphate needed is reduced. It is a matter of economics as to which is used, and in the pilot plant it is cheaper to use ammonia. When the leach is neutralized iron and aluminum hydroxides, molybdenum, arsenic and silicates precipitate. The leach is pumped to a thickener from which the overflow is sent to purification. Five countercurrent thickeners wash the spigot product from the leach thickener, and the washed tails are discarded. Water averaging 5 per cent of the leach volume

TABLE 7.—*Settling of Neutral Leach**

Time, Min.	Settlement, In.	Solution above Solids
15	0	No break
30	6¾	Floccular
40	7¾	Slightly floccular
50	8½	Slightly floccular
60	9	Slightly floccular
75	9½	Slightly floccular
105	9¾	Very slightly floccular

* pH, 6.4; temperature, 42°C.; percentage solids 2.8; sp. gr. sol., 1.17; sp. gr. solids, 2.8.

is added at the head of the washing thickeners. Advance wash solution, containing 75 to 90 grams per liter ammonium sulphate and 16 to 20 grams per liter manganese, flows to the leach thickeners.

The leach contains 2.5 to 3 per cent solids and has a rather slow settling rate, as shown in Table 7.

The sulphuric acid consumption averages 0.25 lb. per pound of manganese leached, owing to the insoluble sulphates, such as calcium, etc., formed in the leach.

An extensive investigation was carried out on the method of removing the leached residue from the solution and washing it free from manganese sulphate and ammonium sulphate. Filtration is not satisfactory, since the large amount of slimes and hydroxides in the residue cause the filter rate to be so slow that it is not economical. A Bird centrifuge was used for several tests, but once again a separation could not be made at an economical rate. Washing in countercurrent thickeners is the most satisfactory method, since they do not require much attention and a washed residue containing less than 1.5 per cent manganese can be obtained.

PURIFICATION

After the manganese has been leached from the ore and the residue removed from the solution, impurities such as As, Co, Ni, Cu, Fe, etc., must be removed before the solution is ready for electrolysis. The purification procedure depends on impurities in the solution. However, it has been found that solution from all the ores tested could be purified by the addition of sulphide ions. Hydrogen sulphide is used in the pilot plant, since it is added easily and is the most economical form of sulphide ion; but barium, sodium, or ammonium sulphides are satisfactory from the standpoint of purification.

The clear overflow from the leach-solution thickeners, which has a pH of 6.4 to 6.6, is stored until ready for use. It flows

from the storage tank to a stainless-steel Nettco Flomix, and hydrogen sulphide is added in the solution line. The Flomix is a totally enclosed double agitator, flanged in the lead-solution line. As the solution flows through the Flomix it is violently agitated, which completes precipitation of the metallic sulphides. As the solution leaves the Flomix, it flows into a surge tank, where it ages 15 to 30 min. and is pumped to a Shriver plate-and-frame filter press. The filter press is precoated with diatomaceous earth, to improve the filter rate.

It was found that the impurities were completely removed if the solution was filtered after 15 to 30 min. aging time. If the precipitated sulphides are allowed to remain in contact with the solution for several hours, re-solution takes place. When the hydrogen sulphide is added to the solution, orange manganese sulphide precipitates; this redissolves and the impurities are precipitated. However, 0.7 to 1.0 gram per liter of manganese is lost as the sulphide during the purification. The hydrogen sulphide necessary to precipitate the metallic impurities completely is 0.10 to 0.15 gram per liter of solution. If any slimes are present in the solution as it comes from the leach thickener, the consumption of hydrogen sulphide is greatly increased, therefore it is necessary to operate the thickener so that there is a minimum of slimes in the overflow. An analysis of the solution before and after sulphide purification is shown in Table 8.

After the metallic impurities have been removed by precipitation as sulphides, the solution contains colloidal sulphur, colloidal sulphides and a small amount of residual arsenic and molybdenum. It was found that the addition of 0.10 gram per liter iron as copperas, followed by oxidation and precipitation of ferric hydroxide, led to adsorption of the colloids, arsenic and molybdenum. The solution, leaving the filter press after removal of the metallic sulphides flows to a brick-lined tank, simi-

lar to the leach tanks, and a solution of copperas is added. The solution is mixed by an Agitair agitator with a hollow shaft. Air is added through the hollow shaft, and the iron is completely oxidized and precipitated. The iron is precipitated in 3500-gal. batches. After all the iron is oxidized and precipitated (which is determined by testing with potassium thiocyanate), the solution is pumped to a storage tank, where it is allowed to age 4 to 6 hr. It is then

phate depends upon a combination of many factors, such as concentration of solution, current density, pH of solution, cathode and anode material, temperature, and rate of flow to cell. It is almost impossible to consider any of these variables separately, since nearly all of them depend on the others, and the limits of one variable cannot be specified without defining the other conditions very closely. It is in this respect that the electrowinning of manganese demands more delicate control than that of other metals, such as zinc and copper.

TABLE 8.—*Purification of Solution*
GRAMS PER LITER

Constituent	Solution before Purification	Solution after H ₂ S Purification	Solution after Fe Purification
Mn.....	35.8	35.1	34.4
(NH ₄) ₂ SO ₄	139.6	139.5	139.2
Cu.....	0.04	0.00008	0.00008
Fe.....	0.003	0.0015	0.0002
As.....	0.0014	0.0006	0.00015
Ni.....	<0.001	<0.001	<0.001
Co.....	<0.001	<0.001	<0.001
Mo.....	0.0005	0.0005	0.0003

filtered on an Oliver precoat drum filter. A mixture of diatomaceous earth and activated carbon removes organic material, which enters the solution with the ammonium sulphate. After filtration, the solution is sent to storage to be drawn into the cell room as needed. Table 8 shows the analysis of the solution before and after removal of iron.

The iron oxidation is carried out at room temperature at a pH of 6.5 to 7.0 and requires 40 to 60 min. to complete the reaction, which can be speeded by heating. As manganese is oxidized, even at a pH of 6.5 to 7.0, there is a precipitation of 0.5 to 1.0 gram per liter of manganese hydroxide. This is not lost, however, as the cuttings from the precoat filter are returned to the leach tank.

ELECTROLYSIS

The successful electrowinning of manganese from relatively pure solutions of manganese sulphate and ammonium sul-

DESIGN OF CELL AND FRAME

The early design of the cell is described on page 2. With the development of the lead-silver anode, it became possible to reverse the position of the anodes and cathodes, owing to the small amount of oxide produced at the anode. The principal advantages gained from this arrangement are: (1) Each cell can be controlled by one feed line instead of the 27 formerly used; (2) all of the cathodes are suspended in a common catholyte, which leads to uniformity of deposition; (3) the catholyte volume is tripled, thereby making control of pH and solution concentrations easier and less critical; (4) as the catholyte volume is so large, the cells may be operated at a higher current density and a larger strip of manganese can be made. This greatly decreases the necessary size of the leaching and purification plant.

The cell design as now used was described previously and shown in Fig. 2. This design was the ultimate result of several different types that were used in the pilot plant. The first cells in the pilot plant were merely a reversal of the anodes and cathodes in the original cell, with tubes leading from the anolyte compartment through the side of the cell for discharge of anolyte. Although this was an improvement, the discharge tubes became plugged, and despite the fact that there was only a small amount of oxide formed, it caused the

diaphragm to bulge at the bottom and touch the cathode after 2 or 3 weeks.

A false bottom was then built into the cells, and the bottoms of the anode compartments were connected with the false bottom by three hard-rubber tubes, which allowed the oxide from the anodes to fall into the false bottom. The anolyte was discharged from the false bottom through a riser pipe at the end of the cell. Although

of 99 per cent lead, 1 per cent silver anodes in small laboratory cells. These anodes markedly reduced the quantity of manganese deposited as oxides at the anode. It was also found that when the area of the anode was made smaller than that of the cathode, with a consequent increase of anode current density, the amount of manganese oxide was reduced further. They reported a ratio of manganese

TABLE 9.—*Results of Anode Tests*

Test No.....	1A	1B	2
Number of anodes.....	16	16	28
Anode analysis, per cent.....	99 Pb, 1 Ag	99 Pb, 1 Ag	98 Pb, 1 Ag, 1 As
Submerged anode area, sq. ft.....	5.32	3.47	3.47
Anode current density, amp. per sq. ft.....	43.3	66.5	81.0
Cathode current density, amp. per sq. ft.....	35	35	45
Hours run.....	330	330	251
Weight of each anode, lb.....	63	38	46
Wet anode sludge formed, lb.....	344	134.5	295.8
Moisture and soluble salts, per cent.....	35.7	35.4	76.0
Dry sludge, lb.....	221.2	86.9	71.0
Mn in sludge, per cent.....	45.6	47.5	58.6
Mn in sludge, lb.....	100.9	41.3	41.6
Mn plated at cathode, lb.....	1304	1496	2756
Ratio anode Mn:cathode Mn.....	0.0774	0.0276	0.0151
Pb lost per Mn plated, lb.....	0.00246	0.00054	0.00010

this was a further improvement, the tubes gradually became plugged.

After several modifications, the present cell was installed and has proved extremely satisfactory. This cell can be operated 6 to 8 weeks, which is the life of canvas diaphragms, without breaking down.

ANODES

An ideal anode for the electrodeposition of manganese would prevent the formation of manganese oxides in addition to having good electrical conductivity and a long life. As manganese is deposited from a sulphate solution, lead was the logical choice of early investigators. It has the disadvantage of causing 1 lb. of manganese to be deposited on the anode for every 4 lb. plated at the cathode. This not only required considerable expense for recovery of the manganese from the oxides but prevented the anodes from being placed inside the diaphragm compartments in the cell.

Woodman and Jacobs⁶ reported the use

deposited at the anode to that at the cathode of 0.0075.

All the anodes in the pilot plant were originally 99 per cent lead, 1 per cent silver, and extensive tests were made in which all of the anodic manganese oxides were carefully collected. The area of the anode was reduced by drilling as many $\frac{1}{8}$ -in. holes in the anode as possible. This reduced the effective area by 40 per cent. It was found later that the addition of 1 per cent arsenic to the lead-silver anode reduced the amount of manganese oxide further. Tables 9 and 10 show the results of comparative tests of lead-silver anodes at different anode current densities and lead-silver-arsenic anodes.

Tests 1A and 1B in Table 9 make it apparent that anodic deposition of manganese is greatly reduced by an increase in anode current density. Test 2 shows the beneficial effect of the addition of arsenic to the lead-silver alloy. Although Tests 1B and 2 are not strictly comparable, since

they were run at different current densities, other tests where Pb—1 per cent Ag and Pb—1 per cent Ag—1 per cent As were compared at the same current density have shown the addition of arsenic to be beneficial. Recent preliminary laboratory tests have indicated that the arsenic content can be reduced to 0.5 per cent without impairing the efficiency of the anode. The

TABLE 10.—*Analysis of Anode Sludge*
PER CENT

Test No.	Mn	Pb	Ag	CaO	MgO
1A	45.6	1.45	tr.	0.41	tr.
1B	47.5	0.93	tr.	0.78	tr.
2	58.6	0.41	0.09	0.63	Not run

substitution of antimony for arsenic gave an inferior anode.

CATHODES

The requirements of a satisfactory cathode for the electrowinning of manganese are insolubility in the electrolyte, low electrical resistance, high hydrogen overvoltage and good flexibility and elasticity.

Since the laboratory results reported by Woodman and Jacobs⁶ recommended the use of aluminum cathodes, these were the first used in the pilot plant. Aluminum has the obvious advantages of low electrical resistance and resistance to corrosion and should be ideal for the deposition of manganese. However, manganese adheres to the aluminum surface very tightly and cannot be removed at all unless a surface treatment is used. Several months were spent investigating various surface treatments, such as oxide films, waxes, oil, fat, graphite, manganese dioxide, sulphides and aluminum powder. All except aluminum powder were unsuccessful. If sufficient surface treatment was given to have any effect on the adhesion of manganese, it would drop from the cathode during electrolysis. If the aluminum cathode was dipped in a suspension of aluminum powder in a volatile agent, such as kerosene, a film

of aluminum powder was left on the cathode. This film did greatly increase the "strippability" of the manganese, but the results were not reliable or consistent enough to warrant being used.

After aluminum cathodes were abandoned, 17 per cent chromium steel was used. This material has the disadvantage of being easily corroded by ammonium sulphate and dilute sulphuric acid; therefore it was very difficult to maintain a smooth finish on the surface of the cathode, which is necessary for efficient stripping of the deposited manganese. It was also necessary to dissolve the manganese remaining on the cathodes after stripping in nitric acid, which resulted in a loss of the manganese. These cathodes had a maximum usable life of 6 months in the pilot plant, and also a very high maintenance cost.

Cathodes of 18-8 stainless steel were next investigated and were very much superior to the 17 per cent chromium steel. The manganese remaining after stripping could be dissolved in spent electrolyte from the cells, thereby recovering the manganese. However, they were subject to slight corrosion, which made it difficult to maintain a finish on the surface of the cathodes from which the manganese could be easily removed. These cathodes had a life of 1½ to 2 years.

Type 316 stainless steel (18 per cent Cr, 8 per cent Ni, 2 per cent Mo) was adopted as the most satisfactory cathode alloy. It is very corrosion-resistant in ammonium sulphate and sulphuric acid and can be maintained economically.

The surface of the cathode sheet must be buffed to a semimirror finish, so that the deposited manganese can be removed easily by flexing or vibrating. If the surface has too high a finish the deposited manganese will peel during the electrolysis, and if the surface is too rough the manganese can be removed only by solution in acid.

An investigation was carried out on the treatment of the cathode surface with

reagents that would leave a film thereon and facilitate stripping. Many materials were used, such as waxes, oil, graphite, silicates, and sulphides. Nearly all of them had a pronounced effect on the adherence of manganese to the cathode surface, but the amount necessary was very critical with all materials except sodium silicate. By immersing the cathode in a solution containing as little as 0.2 oz. SiO_2 per gallon, followed by thorough washing in water, the manganese subsequently deposited was easily removed from the cathode merely by rapping with a rubber mallet. Temperature, time of immersion of cathode, and silicate concentration are not critical as long as the cathode is thoroughly washed in water after immersion. This treatment is effective if the silicate is present alone or in combination with other reagents, such as those in an alkaline cleaner. As the grease must be removed from the cathodes after buffing, the cleaning is done at the pilot plant by immersing the cathodes in a standard alkaline cleaner containing 4.7 per cent SiO_2 (6 oz. per gal.). This procedure not only removes the buffing compound from the cathode but leaves a silicate film that greatly aids stripping of the manganese. By use of the silicate treatment, buffing of the cathodes was reduced from daily to every fourth day, since a rougher finish could be tolerated.

Molybdenum stainless-steel cathodes treated in this manner have been used in the pilot plant for 18 months, and it is believed that they can be used 18 months more before replacement is necessary. The cathodes gradually become so distorted and warped that they must be replaced, but they will have a high salvage value, since there is only a small loss in weight, due to slight corrosion and buffing.

DIAPHRAGMS

Diaphragms are necessary in the electrolytic manganese cell to prevent the sulphuric acid formed from mixing with

the solution around the cathode. At present, manganese can be most economically deposited from solution only by having a pH greater than 7.0. As the acid concentration of the anode does not exceed 45 to 50 grams per liter, it is not necessary that the diaphragm materials be extremely acid-resistant.

A satisfactory diaphragm is one that will resist the acid solution present and have enough porosity to permit passage of current with a low drop in voltage, and allow the solution to flow from the catholyte to anolyte compartment without back diffusion of acid.

Nonwaterproofed canvas (18-oz.) was found to be the most satisfactory diaphragm material. Canvas diaphragms have a life of 6 to 8 weeks, at the end of which time they have rotted and must be replaced. This relatively short life is not serious, however, since calcium sulphate crystals deposit on the diaphragm and gradually reduce the porosity to the extent that the flow of solution is greatly retarded. At the end of 6 to 8 weeks, the diaphragm must be replaced because of the reduced porosity.

Wool, glass, vinyon, and micropore rubber backed with vinyon were tested in the pilot plant. All these materials are very acid-resistant, but since they also must be discarded after 6 weeks because of the deposited calcium sulphate, they have no advantage over canvas. If a cell electrolyte containing no calcium sulphate was used, it would be advantageous to use an acid-resistant diaphragm.

All of the synthetic materials, such as glass, vinyon, and micropore rubber, have 0.1 to 0.3 higher voltage drop than wool or canvas because the wool and cotton fibers are absorbent.

The canvas diaphragms used in the pilot plant are merely bags sewed on the side but with both ends open; one of these is slipped over the anode frame.

Manganese can be electrodeposited over a wide range of cathode current density

with only a small variation in current efficiency and type of deposit. Results of laboratory tests are shown in Table 11.

TABLE 11.—*Effect of Current Density**

Test	Current Density, Amp. per Sq. Ft.	Current Efficiency, Per Cent
1	20	60
2	40	64
3	50	66
4	60	65
5	70	62.8

* Mn in catholyte, 15.0 grams per liter; temperature, 30°C.; pH of catholyte, 8.0; duration of tests, 2 hr.; $(\text{NH}_4)_2\text{SO}_4$, 150 grams per liter (calculated from ammonia content).

The tests shown in Table 11 were made on a short run of 2 hr., to minimize the effect of formation of nodules on the deposit. All deposits were relatively smooth, but there was a slight roughening of the deposit as the density of the current increased. Plates produced in a pilot plant run of 24 hr. at 50 amp. per sq. ft. were quite nodular. The current efficiency was consistently higher than when electrolysis is carried on more than 24 hr., as it decreases more rapidly with time at high current densities than at low current densities, because the area of the deposit has become so great that the actual current density is very low.

Pilot-plant results have shown that at a cathode current density of 45 to 50 amp. per sq. ft. for 24 hr. deposition time, a current efficiency of 60 to 65 per cent will be consistently obtained. The resultant cell voltage is 5.0 to 5.2. The writers believe that these are the most favorable conditions for operating a plant economically when all factors, such as capital investment, labor, and power cost, are considered.

It is to be emphasized that these higher current densities are possible only in the type of cell now being used at Boulder City, in which the cathodes are all in the same common catholyte, because of the ease of controlling conditions of deposition.

SOLUTION CONCENTRATIONS

Cell-feed Solution

The solution fed to the cells contains manganese sulphate, ammonium sulphate, calcium sulphate, magnesium sulphate, and a very small quantity of impurities, of which the total is less than 1 to 2 mg. per liter of solution. Calcium sulphate is present to the extent of its solubility in the solution, which is 1.0 to 1.2 grams per liter, depending on the concentration of the other salts.

Ammonium sulphate is necessary for electrolyzing manganese from sulphate solutions. It prevents the precipitation of manganese in the cell as the hydroxide, acts as a buffering agent, and increases the conductivity of the solution. When plating from a catholyte at a pH of 8.0 to 8.5, the minimum ammonium sulphate concentration in the feed solution necessary to prevent hydrolysis of the manganese is 125 grams per liter. However, for safe operating practice, it should be 135 to 140 grams per liter. As the ammonium sulphate is increased further, however, the deposited metal becomes pitted and current efficiency is lowered. This is shown in Table 12.

TABLE 12.—*Effect of Ammonium Sulphate Concentration**

Test	Ammonium Sulphate, Grams per Liter	Current Efficiency, Per Cent
1	125	64.6
2	150	60.2
3	175	55.9
4	200	52.8

* Catholyte pH, 8.2 to 8.4; Mn in catholyte, 12 to 15 grams per liter; current density, 45 amp. per sq. ft.; temperature, 30°C.

It is desirable from the standpoint of economics to carry as high a manganese concentration in the feed solution as possible, because this will result in the maximum strip in the cell and therefore require a minimum amount of solution, which governs the size of leaching and purification plant necessary. Laboratory results indicated that concentrations of 40 to 50

grams per liter of manganese could be attained successfully; but in the pilot plant it was found that 34 to 40 grams per liter was the maximum that could be used successfully, as plant solutions are subjected to wide variation of conditions such as agitation, evaporation, and temperature.

Although magnesium has no effect upon electrodeposition, it must be controlled to prevent the precipitation of manganese-magnesium-ammonium sulphate. If the MgO content of the solution is kept below 8 grams per liter and the temperature above 25°C. at all times, 40 grams per liter of manganese can be carried in the solution at an ammonium sulphate concentration of 135 to 140 grams per liter. However, for safe operating practice, a manganese concentration of 34 to 36 grams per liter is advisable. Removal of magnesium will be discussed under the section on impurities.

The addition of 0.10 to 0.15 grams per liter of SO₂ to the cell feed was found to be beneficial in preventing hydrolysis of manganese in the solution during handling and storage.

The pH of the solution as it comes from the purification plant is 6.5 to 7.0.

Catholyte and Anolyte

When a cell is put into operation, it is filled with solution containing 135 to 140 grams per liter of ammonium sulphate and 12 grams per liter of manganese. The pH is adjusted to 8.0 with ammonia. As deposition begins, ammonium ions accumulate in the catholyte and sulphate ions in the anolyte. After 4 to 8 hr., the ammonium concentration reaches a constant value greater in the catholyte than the feed solution by 20 to 25 grams per liter reported as ammonium sulphate. There is a corresponding lowering of ammonium concentration in the anolyte during the first few hours, then it rises to a value equal to that in the feed solution. After equilibrium is reached in the cell, these ammonium values remain relatively constant during the life of the

cell. There is a loss of 0.05 to 0.08 lb. of ammonia per pound of manganese deposited by evolution and spray from the cells.

It is desirable to remove the manganese from solution to as low a concentration as possible, not only because less solution is required but to minimize the possibility of formation of manganese hydroxide. Laboratory tests (shown in Table 13) under standard conditions (pH, 8.2; current density, 45 amp. per sq. ft.; and temperature, 30°C.; (NH₄)₂SO₄, 135 grams per liter; manganese in feed, 34 grams per liter) indicated that 12 grams per liter of manganese was the optimum concentration.

TABLE 13.—*Effect of Manganese Concentration in Catholyte on Current Efficiency*

Test	Catholyte Mn Conc., Grams per Liter	Current Efficiency, Per Cent
1	6	47.0
2	8	56.3
3	12	62.3
4	15	59.8
5	19.5	56.9
6	21	43.5

Pilot-plant results, however, have shown that under the same deposition conditions, the catholyte manganese can range from 7.5 to 14.5 grams per liter without a loss in current efficiency. If the manganese is held below 7.5 continuously, burning of the deposit results; and if the manganese is raised above 14.5 grams per liter excessive treeing followed by burning occurs, and formation of manganese hydroxide begins. In the pilot-plant operation the manganese in the catholyte is normally held between 8 to 10 grams per liter, which represents an average strip of 26 grams per liter of manganese from the feed solution to the cell.

The presence of manganese hydroxide in the catholyte is detrimental to the plating operation. Small amounts cause the formation of nodules and trees, which

lower the current efficiency. As the quantity of manganese hydroxide increases, the type of deposit changes from light gray to dark, with a bronze luster, with a continually lower current efficiency and peeling within a few hours. With a further increase of hydroxide, no deposition at all is obtained.

EFFECT OF CELL pH

The hydrogen-ion concentration of the catholyte during electrolysis has a great effect on the type of manganese deposit and current efficiency. In the pH range (6.0 to 8.0) the solution is well buffered by the ammonium sulphate present. Between pH 3.5 to 6.0, the solution is very unstable, and it is almost impossible to maintain a catholyte pH in that range. Table 14 shows the effect of catholyte pH on the type of deposit and current efficiency. These results were obtained in a small laboratory cell under standard conditions (temperature, 30° C.; $(\text{NH}_4)_2\text{SO}_4$, 140 grams per liter; manganese, 12 to 15 grams per liter; current density, 45 amp. per sq. ft.).

TABLE 14.—*Effect of Catholyte pH on Current Efficiency and Deposit*

Test	Catholyte pH	Current Efficiency, Per Cent	Appearance of Deposit
1	2.1	31.5	Bright, re-solution at edges
2	3.4	37.0	Bright, re-solution at edges
3	7.1	54.2	Bright
4	7.65	57.5	Bright
5	8.08	58.8	Light gray
6	8.20	58.0	Light gray
7	8.5	54.5	Dark gray

The results shown in Table 14 were verified in the pilot plant, except that in the pH range 8.1 to 8.4, current efficiencies were consistently between 60.5 and 65.0 per cent. The pilot-plant cells normally operate at an average pH of 8.25 when the temperature is 32° to 36°C. A higher catholyte pH indicates that the cell is not operating normally because of some change in condition, such as manganese or am-

monium sulfate concentration, temperature, or presence of impurities in the solution. If the pH drops below 8.0, it is usually because of leakage of acid from the anolyte compartment through a broken diaphragm.

CELL TEMPERATURE

It is desirable to operate an electrolytic manganese cell at as high a temperature as possible in order to minimize the amount of cooling necessary. The pilot-plant cells are cooled by circulating cold water through lead coils in the cell. Cell temperatures from 25° to 37°C. have been found to have little or no adverse effect on the type of deposit or current efficiency. As the temperature rises above 37°C., the deposited metal becomes very bright and takes on a high luster, and the amount of nodules and trees increases, with a resultant lowering of current efficiency. If the temperature is lowered to 20°C. or below, the deposit is very fine grained; but the conductivity of the solution is greatly decreased. The pilot-plant cells are held within the temperature range 34° to 37°C. Table 15 shows the effect of cell temperature on current efficiency and type of deposit under standard conditions.

TABLE 15.—*Effect of Cell Temperature on Current Efficiency and Type of Deposit*

Test	Temperature, Deg. C.	Current Efficiency, Per Cent	Type of Deposit
1	30	61.5	Light gray, smooth
2	35	62.0	Light gray, smooth
3	40	56.5	Bright, nodular
4	45	48.0	Very bright and nodular
5	50	40.0	Heavily treed and some re-solution

ADDITION AGENTS

An exhaustive study of addition agents was made in an attempt to find one or a combination of several that would decrease the formation of nodules and trees on the deposited manganese and thereby increase

the current efficiency. However, no addition agents were found that had any beneficial effect on the deposit under the plating condition as maintained in the pilot plant, and several were deleterious. Table 16 summarizes the principal reagents tested.

TABLE 16.—*Effect of Addition Agents on Manganese Deposit*

Reagent	Concentration of solution, Mg. per Liter	Effect
Glue.....	5-30	Less than 30 mg., no effect; greater than 30 mg., darkening of deposit
Gelatin.....	Up to 50	No effect
Gum arabic.....	Up to 30	Similar to glue
Goulac.....	Up to 20	Dark deposit at higher concentrations
Ammonium citrate..	Up to 1	No effect
Urea.....	Up to 20	No effect
Dextrose.....	Up to 30	No effect
Karaya gum.....	Up to 20	No effect except dark dep.
Locust bean gum....	Up to 20	No effect except dark dep.
Surface active agents: X-1, Duponol S, Dreft, Tergitol Penetrant 4, etc.	5-200	No effect except froth at high concentration

EFFECT OF SOLUTION IMPURITIES

The effect of impurities depends on so many variables that a complete study of all conditions and combinations would be difficult and extremely prolonged. An investigation was made, however, to determine the effect of certain common impurities as they occur singly. The actual amount of any impurity that can be tolerated is contingent on a number of factors, of which the most important are density and distribution of current, time of deposition, pH and the presence or absence of other impurities. The relative toxicity of the impurities studied is very definite. Three methods were used in the investigation:

1. Two-hour runs were made in a very small cell under standardized conditions, as follows: Mn, 15 grams per liter; total ammonia computed as $(\text{NH}_4)_2\text{SO}_4$, 150 grams per liter; pH, 8.0 to 8.2; tempera-

ture, 30°-32°C. The electrolyte used was regular pilot-plant electrolyte that contained no impurities detectable by chemical means. The concentration of added impurity required to lower the current efficiency 2 per cent was determined. Concentrations of impurities that could be tolerated by this method were larger than those found for longer runs, but the relative toxicity of various impurities agreed with results obtained by the other methods.

2. If a deposit of manganese is started under the usual conditions at a current density of 45 amp. per sq. ft., and the current density subsequently decreased in uniform steps at equal intervals of time, manganese will continue to deposit until a certain minimum current density is reached. Below this current density only hydrogen is deposited, and the manganese redissolves. The detection of this minimum current density by visual inspection of the deposit is tedious and difficult but if the change in potential between the cathode and the solution next to the cathode is measured, there is, in the vicinity of the minimum current density, an abrupt change in potential that is rapidly detected. Although the actual potential values obtained are empirical, inasmuch as the time intervals allowed between changes of current density influence the result, reasonably concordant results were obtained by standardizing the procedure.

The value of this experiment, as far as the present study is concerned, lies in the fact that the presence of those impurities in the electrolyte, which have been found to be harmful, decidedly raises the minimum current density found by this method. Concentrations of impurities that can be definitely detected are lower than in method 1.

3. The ultimate test for the presence of impurities is plating for 24 hr. in an experimental cell under conditions prevailing in practice. This was done in a cell containing one cathode with an area of 0.5 sq. ft.

Plating tests were carried out using the information gained in methods 1 and 2 as a guide in selecting the concentrations of impurities. The amount of impurity that could be tolerated was found to decrease as the plating time increased. The results of these tests are summarized in Table 17.

TABLE 17.—*Effect of Impurities in Cell Solution*

Impurity Added	Maximum Allowable Concentration, Mg. per Liter		
	Method 1	Method 2	Method 3
Co.....	5	1	0.5
Ni.....	5	2	1
Cu.....	10-15	5	5
As (trivalent).....	6-9	1-2	Erratic. Good deposits have been obtained at 8.0
As (pentavalent).....	24	24	24
Ferrous Fe.....	30	20	15-20
Pb.....	No effect up to limit of solubility		
Sb.....	Greater than 5.0		
Ag.....		2	
Zn.....	Greater than 10	20	20

Cobalt and nickel are definitely the most harmful impurities studied. Although the results with trivalent arsenic were not consistent, it is deleterious. Concentration of 5 to 10 grams per liter of zinc may even be beneficial, since higher current efficiencies are frequently but not always obtained.

The appearance of manganese deposits made from solutions containing impurities is not characteristic of the impurity. The first evidence of solution impurity is always a black border around the edge of the deposit. The width of the border increases with time and concentration of impurity, and when the solution is badly contaminated black areas may appear unaccountably in the center of the deposit.

Moderate variations in manganese and ammonium sulphate concentrations do not greatly affect the results obtained from added impurities, but the harmful effect

of impurities is greatly increased by decreasing pH and current density.

Although the presence of calcium and magnesium in the solution has no effect on the electrolysis of manganese, they crystallize out of the solution and plug valves, solution lines and pumps. Calcium sulfate continually precipitates wherever the solution is acid, and magnesium precipitates continually as a triple salt of manganese-magnesium-ammonium sulphate with a resultant loss of manganese and ammonium sulphates. Under normal operating conditions and temperature, calcium is present in the solution to the extent of 0.9 to 1.2 grams per liter as CaO and magnesium 11 to 14 grams per liter as MgO.

Magnesium can be removed as the triple salt by chilling the solution to 10° to 15°C., but for each pound of magnesium removed approximately 2 lb. of manganese and 5 lb. of ammonium sulphate are also removed. It is necessary to recover the manganese and ammonium sulphate. If the triple salt is heated to 300° to 400°C. with an excess of lime, 50 per cent to 70 per cent of the ammonia can be evolved, the remainder being decomposed. After the ammonia has been driven off, 95 per cent of the manganese can be recovered from a solution of the remaining crystals by precipitation as the carbonate. This method of removing magnesium, with subsequent recovery of manganese and ammonium sulphate, is expensive, and it is doubtful whether their recovery would be economical.

Preliminary tests have shown that the calcium and magnesium can be precipitated as the fluorides with only a slight loss of manganese if the quantity of ammonium bifluoride added is controlled. Plating tests on solutions from which magnesium and calcium were precipitated by ammonium bifluoride indicated that the small quantity of residual fluoride left in solution did not affect the plating. However, it will be necessary to cycle solution several times through the plant before it can be definitely

stated that fluorine in small quantities is harmless.

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DISCUSSION

E. M. WANAMAKER.*—The men of the Bureau of Mines are to be congratulated on the excellent paper they have presented dealing with the Bureau of Mines' pilot plant at Boulder City, Nevada.

The Electro Manganese Corporation was organized for the purpose of establishing in this country a business based on the electrowinning of manganese. Although much laboratory and pilot-plant study had been devoted to this subject by the staff of the Bureau of Mines and by others, it was found that many serious problems remained to be solved in connection with the commercial development and refinements of the process. The business so established represents the first commercially successful plant in this country, and probably in the world.

The company was organized in 1938 and started operations the following year. Production had reached a monthly average of more than 99,000 lb. during 1941, when in November of that year the Bureau's pilot plant at Boulder City commenced operations. Obviously, we at Knoxville were primarily interested in securing maximum production at minimum cost, and our research work was necessarily concerned chiefly with actual plant problems.

We have used a great variety of ores, ranging

from Chamberlain and Arkansas carbonates in the early days to our present plant feed of imported high-grade oxides mixed with local oxide tailings plus by-product solution from a near-by chemical plant. The use of carbonate ores proved, in spite of their direct solubility, to be more expensive than reduced oxide ores, because of higher freight costs per unit of manganese coupled with very high acid consumption and large amounts of residue. Most ores can be successfully treated but obviously the lower grade ore mixtures require more equipment for such steps as grinding, reduction, settling, and filtering. Average grade of our ore mixture is 32 per cent Mn.

In the treatment of ore prior to leaching, we use a Raymond roller mill, with air separation, for grinding. As at Boulder City, we dry our ore during the grinding process, a feature that involves a dust problem at both plants. We have developed and built two identical reduction furnaces, which have proved very satisfactory for our needs. Each of the furnaces includes a pair of 12-in. i.d. alloy-steel tubes, 15 ft. long, joined at one end to a 15-ft. length of ordinary 12-in. i.d. wrought-iron pipe. The alloy tubes pass through a chamber heated electrically by Nichrome resistance elements.

The wrought-iron extension is sprayed with water to provide cooling for the reduced ore. Ore and reduction material are fed in at the open end of the alloy tubes and advance by rotation of the tubes through the heating section and into the cooling chamber. The reaction gases leave each tube at the feed end. The exit end is housed to prevent access of air, the reduced ore dropping to a Redler conveyor, which delivers to the storage bin. Each of the two furnaces has a capacity of about 12 tons of ore daily. The furnace permits very close temperature control, which we find to be of great importance when using various ores and ore mixtures. Reduction is consistently of the order of 98 per cent or better, and we have not been troubled with reoxidation.

Our leaching and purification is done by the batch system. There are six leach tanks, each with a capacity of 8000 gal.; and five purification tanks, each of 10,000 gal. capacity.

In the leaching section there are several features that differ from the Boulder City practice. We use lime to raise the pH of the leach from 2.5 to 3 up to the point at which oxidized iron precipitates. Instead of the

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countercurrent Dorr-thickener system for residue washing, we have one 40-ft. Dorr thickener followed by a Moore filter, which in turn is followed by an Oliver filter. As our plant is within the city limits of Knoxville, and the site comprises only $3\frac{1}{2}$ acres, it would have been impracticable from space considerations to use a countercurrent washing system. Furthermore, our residues must be trucked to the dump, and could not be pumped to a pond as at Boulder City. We have had excellent results with our settling and filtering equipment and consider our residue losses to be satisfactorily low, about 3.25 per cent of the Mn to the process. For precipitation of nickel, cobalt, copper, etc., we use ammonium sulphide instead of hydrogen sulphide.

We do not use the ferrous sulphate step as practiced by the Bureau; on the other hand, we utilize particular treatments and procedures for the removal of certain impurities that do not precipitate as sulphides. The purified solution is filtered through Shriver presses, using wooden plates and frames, following which it is ready for the cell room.

Our cell room contains 48 cells in series, each motor-generator cell with 21 anodes and 20 cathodes. Current is supplied by a 1500-kva. motor-generator set, which normally operates at 6000 amp. and nearly 270 volts. Current density is 40 amp. per sq. ft. of cathode area. One cell is cleaned each week day, thus completing a cycle in 8 weeks, which is the life of the diaphragms.

In the matter of cell-room equipment, there is a marked difference between the Bureau's practice and our own. The cell that the Bureau has developed is ingenious, particularly with respect to the unusual feature of separating the two solutions (anolyte and catholyte) in a horizontal plane by means of the false bottom, as also in regard to the open bottom of the anode diaphragm. At Knoxville we use diaphragms around the cathodes and the anolyte fills the cell around the diaphragms.

As mentioned above, numerous problems were encountered in putting the process on a commercially successful basis; among them: (1) control of magnesium in the electrolyte, (2) cell cooling, and (3) evaporation of electrolyte to make room for the leach-residue wash waters.

As regards the first point, it should be noted

that nearly all manganese ores carry magnesium, this being notably true of some of the largest domestic deposits, such as Three Kids, Chamberlain, and Emma mine. As a result, solutions in an electrolytic manganese plant are normally saturated with magnesium and calcium. Unless this magnesium is satisfactorily removed, it will eventually crystallize, and I believe the men of the Bureau will confirm the fact that this usually takes place in the most inaccessible spots, such as pipe lines or pumps. Any appreciable drop in temperature of the plant electrolyte can have disastrous results by causing excessive crystallization.

At Knoxville, the three problems were solved by means including the direct evaporation of solution, for which we circulated a large quantity of cell anolyte over cooling towers. This circulation provides adequate evaporation to make room for residue wash waters, sufficient cooling for holding the cell temperatures down to about 35° to 40°C. , and, most important, crystallizes out, at a place where it can be readily removed, a complex sulphate of Mg, Ca, NH_3 , and Mn, which can be collected periodically and sold as a fertilizer for citrus fruit. The magnitude of the magnesium problem may be judged by the fact that our plant produced 100 tons of the complex salt during each of the last two months. This was partly due to the use of a plant feed relatively high in magnesium.

The outstanding feature of the Boulder City cell—namely, the possibility of feeding catholyte in one relatively large single stream to each cell—as compared with our practice of feeding through 20 individual “spinets,” one to each diaphragm, must be counterbalanced against the previously mentioned advantages obtained by circulating cell anolyte.

After many experiments, we developed our own anode, based on the work of Fink and Kolodney, which has a lead base and contains tin, antimony, and cobalt. This has given excellent results and has a life of over 18 months. Formation of MnO_2 is low, about 2.5 per cent of the Mn to the plant, but this is not lost, as much of it is recovered by reuse in the process. One of the problems solved at Knoxville was the development of a satisfactory cathode and process of using it. The composition of the cathode is about 18 per cent chromium, about 12 per cent nickel and about 2 per cent molybdenum.

There is insufficient time to mention numerous pieces of equipment used, but I might say that rubber-covered steel agitators furnished by the New England Tank and Tower Co. have given good results in the leaching tanks. Equally satisfactory have been the numerous T-4MG Durimet pumps used for circulating electrolyte and the rubber-lined Allen-Sherman-Hoff pumps for moving leach slurry to the Dorr thickener.

Only a few materials have proved satisfactory in resisting the corrosive effect of the electrolyte—for instance, rubber, stainless steel, lead, and wood.

Plant production capacity was approximately 115,000 lb. per month prior to the expansion program carried out in 1942 and early 1943. The expanded plant was intended to produce 230,000 lb. monthly but owing to improved current efficiency, and other factors, the plant has been operating at more than 9000 lb. daily for the last few months. Total production to date has amounted to over 5,750,000 pounds.

I have merely tried to compare the general features of the process as practiced at Boulder and Knoxville. It is both natural and stimulating that we do not agree on numerous details. We would, however, certainly agree on the fact that the broad outlines of the process have been thoroughly investigated and successfully applied on a commercial scale. The process is complex and sensitive and demands the most exacting control to function uninterruptedly.

R. H. CROMWELL.*—During the course of development work at Knoxville, the production rate has been progressively stepped up by the application of inventions and improvements. These improvements have made it possible to maintain a continuous and dependable production of electrolytic manganese.

The progress made can best be indicated by Table 18, showing the amount of electrolytic manganese produced since the plant started.

J. H. JACOBS (author's reply).—Mr. Wanamaker's brief description of the Electro Manganese Corporation's plant practice is very interesting and I certainly do agree that the important phases of the production of

electrolytic manganese have been sufficiently investigated and applied on a large scale to indicate definitely that electrolytic manganese as an industrial product is here to stay.

TABLE 18.—*Electrolytic Manganese Produced at Knoxville*

Year	Pounds	Average, Lb. per Month
1939	43,669	
1940	418,837	34,903
1941	1,190,042	99,170
1942	1,306,310	108,859
1943	2,385,486	196,790
First two months 1944	524,889	262,444

As Mr. Wanamaker indicated, the removal of magnesium is absolutely necessary, because as the concentration increases it eventually reaches the point where it crystallizes as a complex sulphate in the coldest parts of the circuit. Since this paper was written a continuous method for removal of the magnesium has been perfected and put into operation at the Boulder City pilot plant. The method consists of pumping the anolyte or spent electrolyte from the cell room through two 6 by 6-ft. wooden tanks, each containing lead coils through which cold water is circulated. The complex sulphate crystallizes in a fine, granular form as the solution is cooled.

Overflow from the cooling tanks is pumped to a continuous Bird solid-bowl centrifugal filter, where a complete separation of solution and the complex sulphate crystals is made. The sulphate product as discharged from the centrifugal filter contains 2 to 8 per cent moisture. It is then air dried and bagged in 100-lb. lots.

The average analysis of the air-dried product is 4 to 5 per cent Mn, 4 to 5 per cent Mg, 34 to 36 per cent ammonium sulphate and 28 to 30 per cent water of hydration. The water can be driven off at 100°C. It is necessary to cool the solution in the crystallizing tanks to a point slightly lower than any other point in the plant circuit. In the summer at Boulder City this is 19° to 20°C. This ensures removal of the magnesium at the proper place. Cold water for the cooling coils is obtained by use of a spray tower.

This method has proved to be very satisfactory and the only labor involved is for bagging the sulphate product.

* Consulting Engineer, East Orange, N. J.

Climax Conversion Practice

By E. S. WHEELER,* MEMBER A.I.M.E.

(New York Meeting, February 1944)

THE conversion plant of the Climax Molybdenum Co. is at Langeloth, Washington County, Pennsylvania, approximately 30 miles west of Pittsburgh. The molybdenite concentrates converted originate in the company's mine and mill at Climax, Colorado.¹ They are delivered to the Langeloth plant by rail packed in 175-lb. bags.

War production of concentrates at the mill started in 1918 but it was not until about 1920 that any peacetime uses of the metal began to develop. Early conversion of Climax concentrates was mainly into ferromolybdenum, produced for the company by a custom smelter.

CHRONOLOGY OF PLANT DEVELOPMENT

In 1924 a small hand-rabbed roaster was built at Langeloth, the roasted concentrates being used principally in the production of calcium molybdate by a conventional wet method. The size of the original plant is indicated by the fact that during 1925 about 400,000 lb. of molybdenum was converted. In 1925-1926, a multiple-hearth roaster was erected (12-ft. o.d. 8-hearth Nichols-Herreshoff); also the first experimental ferromolybdenum was produced at Langeloth. At this time calcium molybdate was produced in the

furnace by a process to be described. With continued interest in and increased use of molybdenum, it was necessary to arrange for enlargement of plant facilities. Although only one 12-hearth 16-ft. o.d. roaster was erected at this time (1929), plans were prepared for a duplicate unit, which was completed in 1935, giving a potential roasting capacity of some 16,000 lb. Mo per day under the then prevailing roasting practice. Shortly after this second unit had gone into production, increased demand overtaxed the plant, and as a result two 12-hearth 18-ft. o.d. roasters were placed in operation in 1936 and 1937. This gave the plant a potential roasting capacity of 40,000 to 50,000 lb. Mo per day, and necessitated major changes in auxiliary handling equipment as well as improved facilities for producing ferromolybdenum.

Following the introduction (1938) of a new product—molybdic oxide briquets—and because of the constantly growing demand for molybdenum, plant facilities were again enlarged in 1940 and 1941 by the erection of two 16-hearth 18-ft. o.d. roasters. These two new units, along with a change in roasting practice, brought the potential roasting capacity to 150,000 to 190,000 lb. Mo per day, based on about 15 lb. per sq. ft. of hearth area. Other departments of the plant have necessarily grown, until today the plant is modern throughout and completely mechanized, with equipment geared to produce marketable products as follows:

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* Superintendent, Langeloth Plant, Climax Molybdenum Co., Langeloth, Pennsylvania.

¹ E. J. Duggan: Climax Milling Practice. *Trans. A.I.M.E.* (1943) 153, 588.

PRODUCTS	MO CONCENTRATED PER 24 HR.
Roasted concentrates.....	150,000-190,000
Ferromolybdenum.....	30,000- 50,000
"Calcium molybdate".....	40,000- 60,000
Briquets.....	75,000- 85,000
Pure oxide.....	4,000- 6,000
Sodium molybdate.....	800- 1,200

Table 1 gives yearly shipping data in terms of pounds of molybdenum converted at Langeloth, and is an indication of the growth of conversion facilities.

TABLE 1.—Yearly Shipments in Terms of Pounds of Molybdenum

Year	Calcium Molybdate	Roasted Concentrates		Briquets	Sodium Molybdate	Pure Oxide	Ferromolybdenum	Molybdenum Silicide	Total
		Bbl.	Canned						
1924	50,000								50,000
1925	394,135*								394,135
1926	663,504*								663,504
1927	379,306*								379,306
1928	1,137,202	111,237					34,651		1,283,090
1929	1,439,433	122,745					96,262		1,658,440
1930	740,756	109,164					99,416		949,336
1931	443,364	24,634					100,682		568,680
1932	293,304	35,962					119,205		448,471
1933	689,726	49,249					226,600		965,635
1934	1,123,278	42,893					458,329		1,624,500
1935	2,123,940	106,459					924,406		3,154,805
1936	3,410,142	114,971				1,233	1,527,522		5,053,868
1937	3,690,491	2,160,313				9,217	2,542,779		8,402,800
1938	2,666,153	1,211,200				5,678	1,094,128		4,377,609
1939	2,300,012	295,902	382,700	1,608,369		99,672	1,829,438		6,516,093
1940	2,314,928	253,458	1,301,270	2,560,233		228,812	2,853,694		9,512,395
1941	2,859,631	536,811	2,756,725	5,051,700	39,605	264,663	7,393,385	13,365	18,915,891
1942	3,949,142	1,780,800	7,768,265	9,386,344	25,906	143,829	12,875,183	10,779	35,940,248
									100,858,806

* Combined calcium molybdate and roasted concentrates.

The general plant flowsheet, as shown in Fig. 1, will be followed in discussing the various conversion departments.

ROASTING DEPARTMENT

Ore Unloading and Storage

The bags of molybdenite concentrates are moved from car to storage by means of a 325-ft. belt conveyor. Storage capacity is available for approximately 6,000,000 lb. of concentrates. Table 2 gives a typical analysis of concentrates.

Type of Roasting Furnace

The six roasting furnaces, of standard Nichols-Herreshoff design when erected,

have been altered to conform with the changes in roasting practice outlined in the following pages. They are essentially identical except for size.

Preheating is done by means of large natural-gas burners on alternate hearths. These burners are extinguished as the concentrates become well ignited on the respective hearths. The concentrates are fed from a small hopper to one point on the perimeter of the top hearth by means of a

screw conveyor. The shaft speed of the furnace varies with the charge from $\frac{3}{8}$ to

TABLE 2.—Typical Analysis of Concentrates

	PER CENT
Total Mo.....	50
Oxide Mo.....	0.03
S.....	34.40
SiO ₂	8.70
Al ₂ O ₃	1.30
CaO.....	0.02
As and Sb.....	Negligible
MgO.....	0.03
Pb.....	0.05
Cu.....	0.28
Zn.....	0.13
Fe.....	0.53
P.....	tr.
Oil.....	4.47

1 r.p.m., in order to maintain the height of the ridges of ore at about $2\frac{1}{2}$ in. Rings with eight small gas burners on each of the two hearths above the lowest assist in the

removal of the sulphur from the roasted concentrates, which are discharged at 0.05 to 0.25 per cent S.

Present Roasting Practice

Under present practice each hearth of the roaster except the lower two is equipped

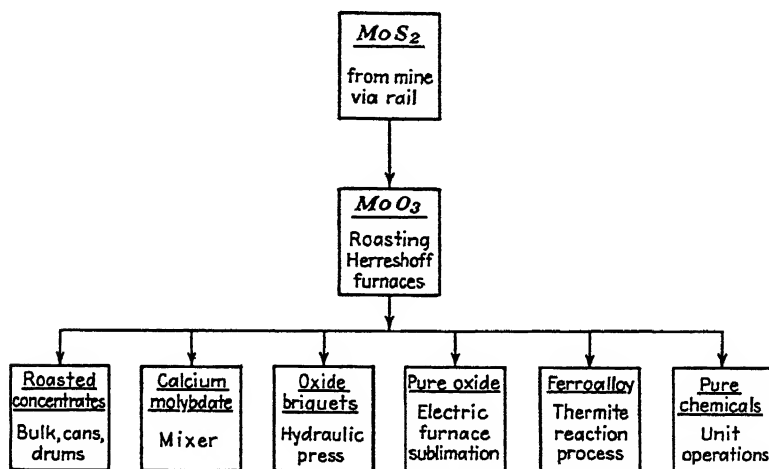


FIG. 1.—FLOWSHEET OF CONVERSION PLANT.

Early Roasting Practice

Prior to 1941 Langeloth roasting practice followed the usual method of exhausting the roaster gases through a single gas outlet from the top hearth. This method placed definite limitations on furnace capacity because of the natural tendency for high temperatures to prevail on the upper hearths. Since molybdic oxide begins to sublime at about 1100°F ., is quite volatile at 1300°F ., and melts at 1463°F ., roasting at temperatures above 1400°F . led to serious operating difficulties, such as wear and corrosion of rabble teeth, plugging of the drop holes and hardening of the permanent bed, as well as excessive losses due to volatilization. The limit of burden under this method of operation was 5 to 8 lb. Mo per sq. ft. of hearth area per day. It was demonstrated that a gas sufficiently high in SO_2 content (4 to 6 per cent) could be made, which, when raised in strength by burning brimstone, could be used in the chamber-process manufacture of sulphuric acid. However, this operation was difficult to control, and was possible only at a real sacrifice in capacity and recovery.

with an individual gas outlet connected to a common vertical header flue extending to the top of the roaster. Hearth temperatures are closely controlled by drawing a large excess of air horizontally across the hearths. Heat above that necessary to maintain roasting temperatures is absorbed by this excess air and immediately removed from the furnace. In general, excessive temperature at a given point is checked by increasing the amount of air admitted to that hearth, or to the next lower hearth. This "spot" regulation is quickly effective and has a minimum effect on other sections of the roaster. Capacity under this system is limited chiefly by the draft available, and by mechanical limitations of the furnace. At a given speed of rotation the burden may be increased until the roast "tails out" at the desired point, which at present is the 10th or 11th hearth on a 12-hearth furnace, and the 14th or 15th hearth on a 16-hearth furnace.

The principal disadvantages of this method of drafting is the heavy dust load occasioned by the large volume of gases sweeping the hearths. To maintain con-

stant temperatures, any increase in charge is accompanied by an increase in draft, which further increases the dust load. Recovery, therefore, is dependent on efficient

charge of 20 lb. Mo per sq. ft. of hearth area per day at 1 per cent SO_2 . Each Multiclone is equipped with a paddle-wheel type fan of capacity slightly exceed-

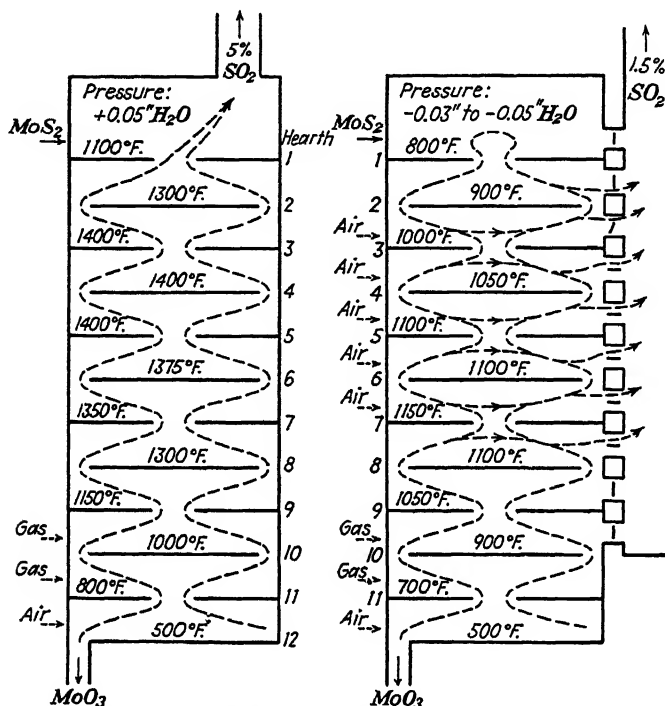


FIG. 2.—FLOWSHEET OF ROASTING FURNACES BEFORE AND AFTER CHANGE.

dust collection. At a charge of 15 lb. per sq. ft. of hearth area per day the dust load is roughly 18 per cent of the charge. The dust contains a ratio of about 95 per cent MoS_2 and 5 per cent oxides. Sublimed oxide is negligible at the prevailing temperatures.

Fig. 2 shows typical hearth temperatures under the past and present methods of roasting.

The gases pass from the vertical flue to Multiclone dust collectors, and then are exhausted into a 500-ft. brick-lined concrete stack. The Multiclones are of vane type with 9-in. tubes, and operate at 600° to 700°F. The dust collector for each furnace is designed to handle the gases from a

ing that of the collector. The Multiclone fans all exhaust into a common horizontal header flue which leads to a double-inlet booster fan of 150,000 cu. ft. per min. capacity, which in turn exhausts the gases into the 500-ft. stack.

Fig. 2 also shows the flow of gases within the furnace. Under the present system of roasting, the outlet dampers on the first and second hearths are generally closed to hold the temperature below the ignition point (900°F.) of the residual flotation oils in the concentrates. However, the temperature is sufficient to vaporize most of the oil, which is then drawn into the flue through the next lower outlet.

Operating Difficulties

Operating difficulties are minimized under this system of roasting. Cleaning of the furnace drop holes, central shaft and

the length of a furnace campaign was limited to the life of the rabble teeth. After a maximum of about six months, therefore, the furnace had to be shut down

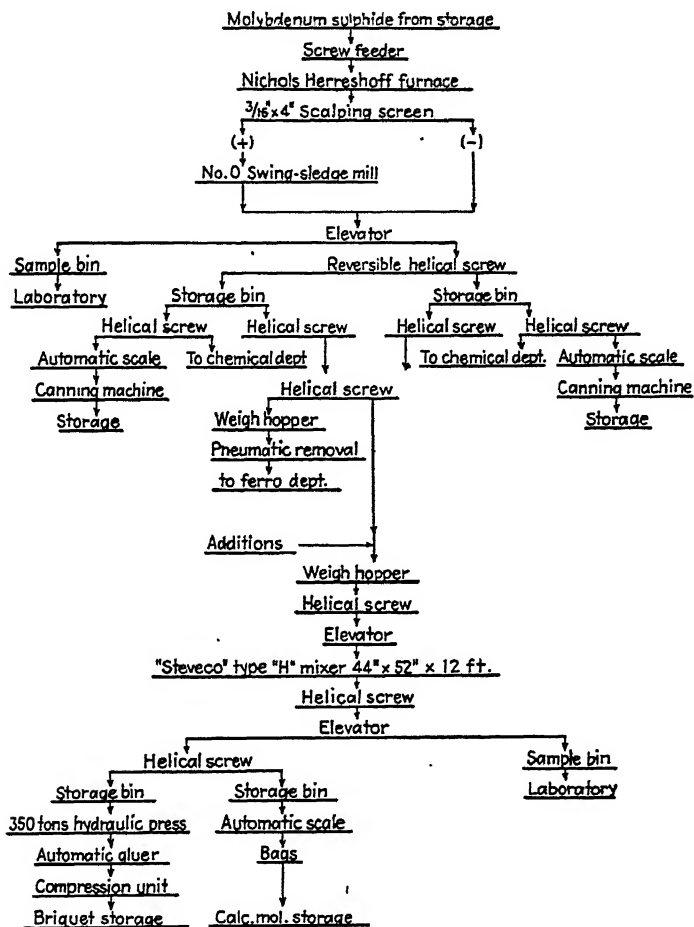


FIG. 3.—FLOW SHEET FOR PRODUCTION OF ROASTED CONCENTRATE.

rabble arms is not difficult. The lower temperatures prevailing allow the permanent bed to be "plowed," and the deposit on the side walls may be cut out by means of a specially designed tooth, which is attached to the rabble arm. Under the temperature conditions of the former method of operation (over 1400°F. on some hearths) the deposit on the bed and walls hardened too rapidly to permit this, and

and completely cleaned out with air hammers and chisels before being re-toothed for another campaign. However, under present conditions, a regular hearth-plowing and side-wall cleaning schedule permits the changing of rabble teeth with no interruption of production, thus extending the length of the campaign indefinitely. The lower temperatures also allow the use of white-iron teeth (alloyed with 0.50 per

cent Cr and 0.25 per cent Mo for toughness), whereas at the temperatures of the former method iron teeth with 28 per cent Cr were necessary.

Handling, Storage and Sampling of Roasted Concentrates

The roasted concentrates are discharged from the furnace by gravity over an inclined screen (opening $\frac{3}{16}$ by 4 in.), the oversize going through a hammer mill equipped with $\frac{1}{4}$ -in. grids. The crushed oversize joins the undersize at the bottom of a vertical bucket elevator, which discharges over a pipe sampler into a screw conveyor, which, in turn, discharges into lot-storage bins. There are two storage bins per furnace, each with sufficient capacity for 24 hr. of production. Approximately 5 per cent of the furnace production passes via the sample pipe into a small sample bin. This sample is further cut through a Jones sampler, and prepared for the laboratory each 24 hr. The analysis of this sample constitutes the lot assay upon which packing and subsequent conversion operations are based.

Fig. 3 shows the flow of concentrates through the furnace and to the storage bins. This figure is also referred to in discussing the flow of roasted concentrates from the lot-storage bins, through various conversion steps. The flexibility of the binning system is indicated by the fact that all furnace storage bins are so connected to a main haulage screw conveyor that roasted concentrates can be drawn from any bin into centrally located weigh hoppers, from which they can be transferred to the desired conversion department.

Technical Molybdc Oxide

The roasted concentrates, or molybdc oxide, are the end product of the roasting operation, and the raw material for subsequent conversion operations. Approximately 70 per cent of the oxide produced receives further treatment. The remainder

is marketed as "technical oxide" packed in 500-lb. barrels, 250-lb. fiber drums, or metal cans.

The analysis range of technical molybdc oxide is as follows:

	PER CENT
Mo.....	56 -62
S.....	0.02- 0.25
Insoluble.....	5.00-11.00
Fe.....	0.50- 1.00
Cu.....	0.15- 0.75
CaO.....	0.05- 0.20
ZnO.....	0.10- 0.20

The oxide is packed into the larger containers directly from the lot bins, the material being screened and then weighed on accurate platform scales. The metal cans are filled by means of automatic scales, which discharge into each can sufficient oxide to contain 20-lb. Mo per can, the gross weight varying according to the lot analysis.

Technical oxide and "calcium molybdate" packing machines are equipped with individual bag filters, thus collecting the dust at its point of origin. Each briquet press is equipped in a similar manner, the dust collected in this operation being returned directly to the circuit.

"Calcium Molybdate"

Calcium molybdate originally was prepared at Langeloth by mixing roasted concentrates with quicklime and water in correct proportions to form a mud, which when heated in a furnace reacted to form technical calcium molybdate, containing about 40 per cent Mo. This material was crushed and packaged in bags containing 5 lb. of molybdenum.

About 1926 the method was changed. Lime was introduced to the hearth directly below the "tailing-out" point and heat was applied, causing a partial reaction to take place, which converted a varying proportion of the oxide to calcium molybdate. The uniformity of the product depended

entirely on the even feeding of the lime and the thoroughness of the mixing on the four hearths and in the elevating equipment and bins. This method required close control.

Later developments disclosed the interesting fact that uncalcined pulverized limestone of high quality, when thoroughly mixed with roasted concentrates, gave a product suitable for additions to steel furnaces. This led to the abandonment of the addition of lime directly to the roasting furnace, and resulted in increased roasting capacity, because the "tailing-out" point could be allowed to move down to the 11th hearth instead of the 8th on a 12-hearth furnace.

"Calcium molybdate" is now prepared by mixing an accurately weighed amount of roasted concentrates of known molybdenum content with sufficient pulverized limestone to give a product analyzing from 42.4 to 42.6 per cent Mo. After thorough mixing the charge is elevated to a packing bin, from which it is drawn through an automatic scale set to deliver 11.8 lb. of product, or 5 lb. Mo. Each bag is check-weighed before sealing. Paper bags of double wall construction are used in the packaging operation.

Molybdc Oxide Briquets

Since the introduction of molybdc oxide briquets in 1938, the use of this product has increased until today the plant is equipped with two hydraulic briquetting presses having a combined capacity of 60,000 to 80,000 lb. Mo per day.

In the preparation of molybdc oxide briquets roasted concentrates of known molybdenum content are thoroughly mixed with air-floated pitch. This mixture is elevated to a bin from which it feeds by gravity to the hydraulic press. The press is a 350-ton capacity, fully automatic, electrohydraulic machine, upward acting, automatically charging the molds, with automatic control of the forming pressure, automatic ejection of the formed briquets,

and provided with an off-bearer for removing the briquets from the machine. A pressure of 18,000 lb. per sq. in. can be applied to each briquet, but average operation calls for 10,000 to 11,000 lb. per sq. in. The mold liners in which the briquets are formed are chromiumplated on the inside to withstand abrasion; about 100,000 briquets can be obtained from a set of liners before replating. Four 4-in. diameter briquets are formed per cycle of operation. The length, and hence the weight of the briquet, is varied according to the analysis of the mix, so that each briquet contains 2.5 lb. Mo. The normal briquet is 4 to 4½ in. long and weighs 4½ to 5 lb., the mix containing 50 to 55 per cent Mo. The four briquets drop from the press into a corrugated box; are check-weighed on an accurate table scale, and pass into a closing machine that glues, seals and counts each box.

Pure Molybdc Oxide

In the preparation of pure molybdc oxide advantage is taken of the characteristic of MoO_3 to volatilize when heated above a temperature of about 1100°F. Technical oxide is fed in a thin layer to the sand hearth of a doughnut-type furnace. The hearth moves under Globar heating elements operating at about 2200° to 2300°F., giving a hearth temperature of 1800° to 1900°F. Considerable MoO_3 is absorbed by the hearth, which soon becomes saturated. Air is drawn in over the heated surface and sweeps the MoO_3 vapors through ports in the outer perimeter of the furnace into a metal flue leading to a bag filter, where the pure MoO_3 is collected. The charge on the hearth makes one pass under the heating elements, and the tailings are then discharged by means of a double-flight cutting and conveying screw. The tails from this operation are still rich in molybdenum and are suitable for use as raw material in other processes. The loss in weight of the charge is about 60 per cent.

Densification

The pure MoO_3 is an exceedingly fine, light product averaging about 99.975 per cent MoO_3 . The major portion of the pro-

duction is densified before packaging. They allow use of the full power with any voltage step. All secondaries are connected with four panels (two for each transformer) where the proper

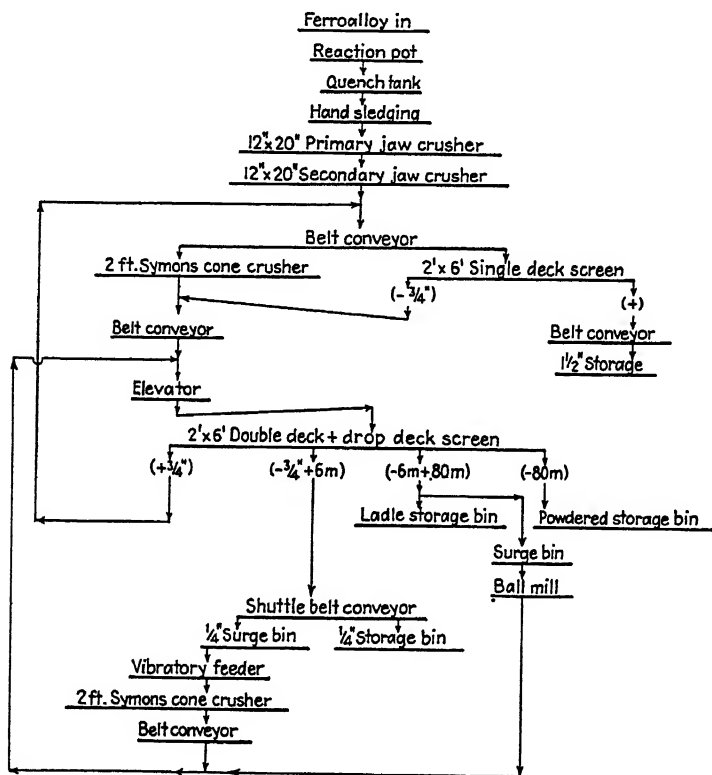


FIG. 4.—FLOWSHEET OF FERROALLOY CRUSHING.

duction is densified before packaging. This is accomplished by “pugging” with a minimum amount of distilled water, followed by drying. The density is increased about seven times in this operation.

Power

The heating elements in the distillation furnace are 29 Globar units, type AT, 82 in. long and 1 5/8-in. diameter. The electrical power for the heating elements is furnished by two 350-kva. transformers in Scott connection, which are fed by three-phase current of 25,000 volts and have two-phase secondary voltages ranging from 155 to

voltages are selected by tap switches. Circuit breakers between the panel and the furnace allow one half of the furnace to be shut off without affecting the other half. One half of the Globar elements in each of the two half circles is connected with one transformer, the other half with the second transformer. This arrangement allows an even load distribution in the primary circuit under all conditions. To increase the life of the Globars four “booster transformers” of 47-kva. output are connected in the secondary lines, which add or subtract 60 volts. At reduced current loads

they can be used to supply 80 volts differential.

Temperatures in the furnace are controlled by two recording pyrometers, the thermocouples for which are placed between two Globars and directly above the center of the hearth, one in each half.

PRODUCTION OF FERROALLOYS

Ferromolybdenum

The first alloy produced at Langeloth was by the thermite process, which is still the method used. Heats of 50 and 100 lb. contained molybdenum were first attempted, but over the intervening years the unit of operation has grown until today 1300-lb. contained heats are produced. A typical thermite mix to produce a 1300-lb. heat is: 1300 lb. Mo in oxide; 116 lb. Al, 93 per cent grade; 1122 lb. FeSi, 50 per cent grade; 618 lb. iron ore, 69 per cent grade; 160 lb. lime; 50 lb. fluorspar, 95 per cent grade.

The roasted concentrates are transferred from the roasting department to the storage bins in the smelting department by means of a pneumatic conveyor. Storage capacity for 650,000 lb. of oxide is available.

Raw materials coming into the plant for the alloy department are also conveyed to bin storage by means of a pneumatic conveyor. The storage bins in the Alloy Department are connected to a central weighing hopper by a system of screw conveyors. Thus the proper amounts of each raw material for the thermite mix can be drawn directly from their respective bins by the operator stationed at the weighing hopper. The weighed batch is then elevated to the top cone of a three-cone mixer, and is mixed by coning action as it drops to the second and then to the third hopper. The mix finally is discharged into a feed hopper, which is lifted over a bottomless brick-lined steel shell, previously set over a shallow pit scooped in wet sand. The mix is run into this reaction pot, the dust hood is set and the pot banked with sand, then the

reaction is started by igniting the charge with a starting fuse made up of a mixture of aluminum and sodium peroxide. The fumes and dust from the smelting reaction are drawn off by fans, through the hood, to a cooling or settling chamber and then to a bag filter, where the major portion of the dust is collected. This dust analyzes about 23 to 25 per cent Mo, and is returned to production in other products.

When the smelting reaction is complete (15 to 20 min.), the slag is tapped by lifting the pot, the bottom of the drain being just above the metal line so that a layer of covering slag remains on the liquid metal. After 4 to 6 hr. the metal has solidified and is removed from the pit by means of crane-operated tongs. The skull of sintered sand that forms on the button of metal is knocked off and the alloy is quenched in water. When cool (2 to 4 hr.) the slag is removed from the top of the metal button, which weighs about 2000 lb. This drastic quenching operation not only cools the metal but also produces fine fractures, which greatly facilitate hand-sledging to pieces of convenient size for handling.

Slag and skulls go to the slag dump for storage, pending further treatment for the recovery of their metal values.

Crushing Circuits

Climax markets four sizes of ferromolybdenum:

1½-in.....	Minus 2 plus ¾ in.
¾-in.....	Minus ¾ in. plus 6 mesh
Ladle size.....	Minus 6 plus 80 mesh
Powdered.....	Minus 80 mesh and down

Fig. 4 is a diagrammatic sketch of alloy production. Two duplicate crushing circuits are maintained.

The first crushing units in the line are two "overbuilt" 12 by 20-in. jaw crushers. The metal is fed by hand to the first crusher and discharged by gravity to the second, which is set to produce the 1½-in. grade. This product is carried by belt conveyor to

the 2-ft. cone adjusted to deliver a minus $\frac{3}{4}$ -in. metal. If $1\frac{1}{2}$ -in. product is desired, the stream of metal from the second jaw crusher is directed over a $\frac{3}{4}$ -in. screen, the

the flow of material in the open boot of the bucket elevator and again passes over the drop-deck screen.

When necessary, the production of pow-

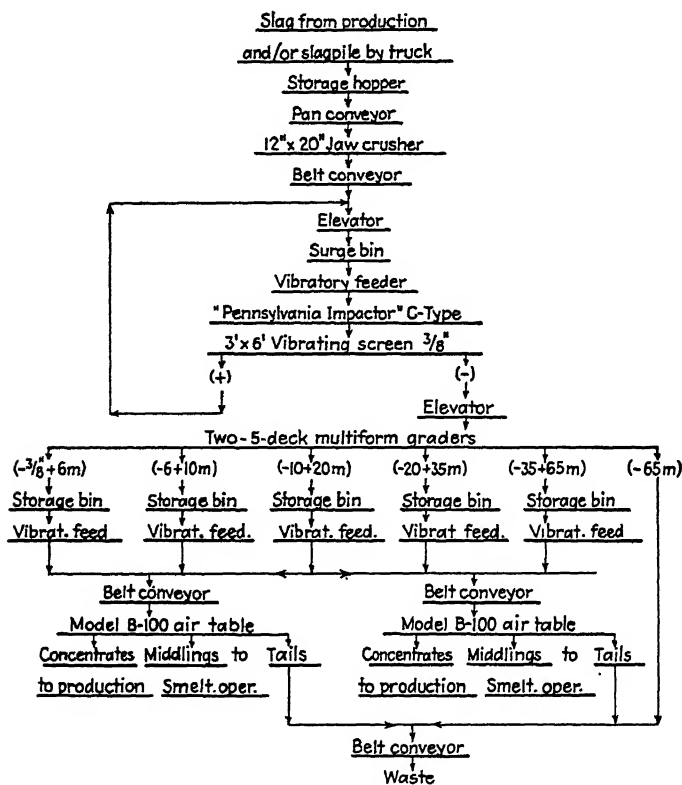


FIG. 5.—FLOWSHEET OF SLAG RECOVERY.

undersize going directly to the cone-crusher discharge chute.

The minus $\frac{3}{4}$ -in. alloy is carried by belt conveyor to the open boot of a vertical bucket elevator, which discharges onto a drop-deck screen where the various sizes ($\frac{1}{4}$ -in., ladle and powdered) are separated and flow by gravity to their respective storage bins. Shipping containers are filled directly from these bins.

The supply of minus 6-mesh material (ladle size) is supplemented by feeding $\frac{1}{4}$ -in. alloy from a surge bin to a second cone crusher adjusted to produce minus 6-mesh. The product from this mill joins

dered alloy can be supplemented by grinding ladle size or $\frac{1}{4}$ -in. metal in a ball mill and again passing the discharge from the mill over the drop-deck screening unit. The ball-mill discharge trunnion is hooded and a considerable portion of the powdered alloy is picked up and caught in a small-unit bag filter.

The specification to be met in producing ferromolybdenum is as follows: Mo, 58 to 64 per cent; Si, 1.50; S, 0.25; C, 0.10; P, 0.05; Al, 0.10; Cu, 0.25.

Dust is collected at the jaw crushers, cone crushers, ball mills and screens by means of bag filters and cyclone collectors.

All screens and hoppers are hooded or enclosed. Dusting and high temperatures are greatly reduced by a monitor-type roof, which extends over the entire crushing and smelting bays.

Molybdenum Silicide

Another alloy produced at Langeloth is molybdenum silicide. A typical mix is given in Table 3, which also shows a typical analysis of the product. Only one grade is marketed, corresponding to ladle-size ferromolybdenum.

TABLE 3.—*Typical Molybdenum Silicide Mix and Resultant Metal Analysis*

Mix	Typical Metal Analysis, Per Cent
1000 lb. in oxide	Mo..... 60
250 lb. aluminum	Si..... 34
760 lb. ferrosilicon, 90 per cent grade	Fe..... 4
166 lb. ferrosilicon, 50 per cent grade	S..... 0.04
50 lb. fluorspar, 95 per cent grade	Cu..... 0.42
160 lb. quicklime	Al..... 0.37

Crane Facilities

One 7½ and one 5-ton crane are maintained over the smelting pits. A third crane of 5-tons capacity serves the crushing circuits to facilitate repair work.

SLAG TREATMENT

The slag from alloy production has been allowed to accumulate but is soon to be treated for its metal content. A completely

new plant has been erected to handle current production as well as considerable tonnages from the slag pile.

The crushed slag will be sized for bin storage and then fed to air tables. Several cuts of metal or metal-containing material will be made, the major portion of the table discharge going to the tailings dump. The metal concentrates from this tabling operation will go into production; the other metallic materials are to be recirculated back to the smelting cycle. Fig. 5 is a diagrammatic sketch of the slag-recovery plant.

CHEMICALS

At present the plant has one producing unit for making sodium molybdate. The process is a conventional one, the sodium molybdate being produced by dissolving technical-grade molybdic oxide in caustic soda, filtering, evaporating, crystallizing and drying.

ACKNOWLEDGMENTS

Thanks are due Mr. Arthur Linz, Vice President, and Mr. M. W. Murphy, Plant Manager of the Climax Molybdenum Co. of Pennsylvania, for the opportunity to prepare this paper and for assistance in obtaining much of the data. Also, special thanks are due Mr. R. N. Carroll, Roasting Superintendent; Mr. D. G. Downer, Smelting Superintendent, and Mr. Jack Noy, Electrical Engineer, for their many helpful suggestions and assistance in its preparation.

Electric Smelting of Cle Elum-Blewett Pass Nickeliferous Iron Ore

By S. F. RAVITZ* AND VIRGIL MILLER,* MEMBERS A.I.M.E. AND F. B. PETERMANN†

(New York Meeting, February 1944)

THE Cle Elum nickeliferous iron deposit is in Kittitas County, Washington, in a rugged, mountainous region about 23 miles north of the town of Cle Elum. The Blewett Pass deposit, which is similar in character and occurrence, is in Chelan County, about 18 miles east of the Cle Elum deposit. A more or less continuous ore zone may extend between the two deposits, since iron ore is reported to have been discovered at Iron Mountain, which lies directly between them.

The ore probably was formed by metamorphism of laterite resulting from leaching of serpentine derived from peridotite. It consists largely of magnetite grains distributed through a matrix of limonitic material containing a small amount of hematite and chromite. Many of the chromite grains have shells and inclusions of magnetite. The magnetite grains range in size from 1200-mesh to $\frac{1}{4}$ -in., the average size being 48 to 65-mesh; the chromite grains range from 20 to 150-mesh. The gangue minerals are olivine and serpentine with a small amount of chlorite, and appear both as very thin bands in the ore and as minute fragments in the limonitic matrix. The nickel is present as minute inclusions of a nickel silicate mineral within the magnetite and gangue par-

ticles, varying in size from 1500 to about 280-mesh.

Detailed analyses of 3000-lb. lots of Cle Elum and Blewett Pass ore are given in Table 1.

TABLE 1.—*Detailed Analyses of Ore Samples*
PER CENT

Constituents	Ore from	
	Cle Elum ^b	Blewett Pass
Cr.....	2.23	2.12
Ni.....	1.43	0.95
Fe.....	52.9	41.4
SiO ₂	5.6	13.4
CaO.....	0.3	0.8
MgO.....	4.1	7.5
Al ₂ O ₃	7.0	2.9
P.....	0.022	0.034
S.....	0.01	0.02
Mn.....	1.1	0.4
Ba.....	nil	
Co.....	0.02	0.02
Cu.....	0.02	0.03
As.....	0.03	
Au.....	nil	
Ag ^a	0.58	
Pt.....	nil	
Fe ⁺⁺	8.9	5.9
Fe ⁺⁺⁺	44.0	35.5

^a Ounces per ton.

^b Spectrographically absent: B, W, Mo, Ta, V, Ti, Bi, Pb, Sb, Sn, Be, In, Hg, Zn, Zr, Cd.

PRELIMINARY TESTS

Attempts to beneficiate the ore by ore-dressing methods, including various combinations of sink and float, tabling, jigging, flotation, and magnetic separation, were consistently unsuccessful. A wide variety of roasting and leaching tests were made on both raw and reduced ore, but in most of the tests little or no nickel was extracted, and in none did the extraction exceed 50 per cent. No nickel could be volatilized as the carbonyl by treating reduced ore with carbon monoxide. Fairly good sepa-

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ration of nickel was obtained by smelting the ore with pyrite, gypsum, or chalcopryrite, but the metal products containing the nickel were so low in grade and contained so much sulphur that subsequent treatment would have been difficult. The best results were obtained by smelting the ore in small clay crucibles with sufficient coke to reduce all the nickel and only a small proportion of the iron; in this manner metal buttons containing up to 30 per cent nickel and no chromium were produced, together with slags containing less than 0.01 per cent nickel.

ARC-FURNACE SMELTING TESTS

In view of the excellent results obtained in the partial reduction tests in small crucibles, smelting tests on a scale of 100 to 150 lb. of ore were made in a 200-kw. type U Lectromelt arc furnace, 24 in. in diameter inside the magnesite lining. The charge constituents were crushed to minus $\frac{1}{4}$ -in., and a pound or two of coke (which was considered part of the charge) was used to start the arc. The smelting time was usually 60 to 90 min., and the pouring temperature 1550° to 1650°C.

Partial Reduction of Ore

Iron-nickel alloys of virtually any desired nickel content can be produced by careful control of the amount of coke used. In a series of 15 tests with 7.5 to 8.5 per cent coke (based on weight of ore) and no flux, metal buttons containing 8 to 22 per cent nickel were produced; the results of a typical test are given in Table 2.

The carbon content was usually 0.02 per cent or less, the silicon and phosphorus 0.01 to 0.02, the sulphur 0.06 to 0.09, and the chromium less than 0.01. The slags contained 44 to 52 per cent Fe, 1 to 4 per cent CaO, and about 9 per cent SiO₂, 15 per cent MgO, and 11 per cent Al₂O₃; the high MgO content was due to absorption of MgO from the magnesite lining. The average nickel content of the slag

was about 0.05 per cent (corresponding to a loss of about 5 per cent), but six of the slags contained 0.01 per cent or less, indicating that the nickel in the slag was probably present as minute prills of metal.

TABLE 2.—*Results of Typical Partial Reduction Test*

Charge: Ore, 100 pounds; coke (0.40 per cent S), 7.5 pounds

Constituent	Analysis, Per Cent		
	Ore	Metal	Slag
Cr.....	1.71	tr.	1.85
Ni.....	0.92	12.4	<0.01
Fe.....	50.5		48.2
SiO ₂	8.4		7.0
MgO.....	2.9		15.9
C.....		<0.02	
Si.....		0.01	
P.....		0.01	
S.....		0.07	
	Reduced, Per Cent		
Cr.....		<0.01	
Ni.....		>99.9	
Fe.....		12.9	

Losses of nickel in the slag become serious when the nickel content of the metal rises much above 20 per cent. For example, about 90 per cent of the nickel was recovered at 30 per cent grade, 75 per cent at 40 per cent grade, and 50 per cent at 58 per cent grade.

Smelting of Slag

The iron and chromium in the nickel-reduction slag can readily be recovered by smelting the slag with an excess of coke. In a test in which a slag containing 47.0 per cent iron and 1.9 per cent chromium was smelted with about 25 per cent its weight of coke and sufficient lime to give a slightly basic final slag, 96 per cent of the iron and 96 per cent of the chromium were reduced to metal containing 3.7 per cent Cr, 3.4 per cent C, and 2.8 per cent Si.

Since only a limited market probably would exist for the chromium cast iron obtained by complete reduction, tests were

made to determine how much of the iron could be reduced as a low-carbon steel. The results of two tests are given in

TABLE 3.—*Controlled Reduction of Slag*
Charge: A. Slag, 100 pounds; coke (0.3 per cent S), 10 pounds; dolomite, 40 pounds.

B. Slag, 100 pounds; coke (0.4 per cent S), 12 pounds.

Constituent	Nickel Slag	Dolomite	Metal	Final Slag
Charge A. Analysis, Per Cent				
Cr.....	2.63		1.37	2.46
Fe.....	38.6	0.5		7.8
SiO ₂	20.8	0.9		27.2
CaO.....	1.6	31.8		17.0
MgO.....	12.1	22.0		30.8
C.....			0.03	
Si.....			0.04	
P.....			0.05	
S.....			0.04	
Charge A. Reduced, Per Cent				
Cr.....			17.0	
Fe.....			82.3	
Charge B. Analysis, Per Cent				
Cr.....	1.80		2.22	1.48
Fe.....	46.5			6.3
SiO ₂	9.4			21.2
CaO.....	3.1			4.0
MgO.....	14.2			47.1
C.....			<0.02	
Si.....			<0.001	
P.....			0.04	
S.....			0.03	
Charge B. Reduced, Per Cent				
Cr.....			59.0	
Fe.....			93.3	

Table 3. The results show that more than 93 per cent of the iron and almost 60 per cent of the chromium can be reduced to a metal low in carbon, silicon, phosphorus, and sulphur.

Production of Stainless Steel

Two 40-lb. ingots of 18-8 stainless steel were prepared by alloying several nickel-iron buttons, having an average nickel content of about 11 per cent, with standard 70 per cent low-carbon ferrochrome in an induction furnace. The analyses of the ingots are given in Table 4.

The tensile properties of the products compared favorably with published data on low-carbon stainless steel, and samples

TABLE 4.—*Analyses of Stainless-steel Ingots*
PER CENT

Constituent	Ingot 1	Ingot 2
Cr.....	18.25	17.40
Ni.....	7.75	7.50
C.....	0.02	<0.02
Si.....	0.13	0.12
P.....	0.018	0.023
S.....	<0.01	<0.01
Co.....	0.49	0.43
Cu.....	0.10	0.10
Mn.....	<0.01	<0.01

left in a standard salt-spray bath for over a month showed little or no corrosion.

CONCLUSIONS

1. The Cle Elum-Blewett Pass nickeliferous iron ore is not amenable to concentration by ore-dressing methods or to treatment by a wide variety of roasting and leaching methods.

2. By smelting the ore in an electric-arc furnace with a deficiency of coke for complete reduction, virtually all the nickel can be recovered as a nickel-iron alloy containing up to 20 per cent nickel. Alloys of much higher nickel content can be produced, but the losses of nickel in the slag become appreciable when the nickel content of the metal is much above 20 per cent.

3. The properties of 18-8 stainless steel prepared by alloying the nickel-iron alloy with ferrochrome compare favorably with those of commercial stainless steel.

4. Nearly all the iron and chromium in the nickel-reduction slag, which usually contains 40 to 50 per cent iron and 2 to 3 per cent chromium, can be recovered as a chromium cast iron by smelting the slag with an excess of coke and with sufficient limestone to form a basic final slag.

5. By smelting the nickel-reduction slag with a carefully controlled amount of coke, more than 90 per cent of the iron

and about 60 per cent of the chromium can be recovered as a low-carbon steel containing more than 2 per cent chromium.

ACKNOWLEDGMENTS

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Antimony—Its Metallurgy and Refining in Recent Years

By CHUNG YU WANG* AND GUY C. RIDDELL,† MEMBERS A.I.M.E.

(Cleveland Meeting, October 1944)

THERE are found in nature upward of 112 minerals containing antimony, but only a few of them, listed in Table 1, can be considered as antimony ore-forming minerals.

Stibnite (Sb_2S_3), antimony sulphide or glance, is the principal ore of antimony. The oxide ores—cervantite, kermesite, valentinite, sernarmontite—occur sparingly in nature.

mony, and the refined metal itself is called antimony "regulus."

The different processes for the treatment of antimony ores are shown in the diagram of Fig. 1.

LIQUATION OF CRUDE ANTIMONY

The first step in the smelting of antimony is a simple one, the process of "liquation," which produces crude or

TABLE 1.—*Antimony Ore Minerals*

Class of Mineral	Name of Mineral	Formula	Antimony, Per Cent	Specific Gravity	Mode of Occurrence
Sulphide	Stibnite	Sb_2S_3	71.4	4.52-4.62	Hypogene
Oxide	Valentinite (rhombic)	Sb_2O_3	83.3	5-5.66	Supergene
Oxide	Sernarmontite (cubic)	Sb_2O_3	83.3	5.22-5.30	Supergene
Oxide	Cervantite	Sb_2O_4	78.9	4.084	Supergene
Hydroxide	Stibiconite	$\text{Sb}_2\text{O}_4 \cdot \text{H}_2\text{O}$	74.5	5.1-5.28	Supergene
Oxysulphide	Kermesite	$2\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$	75.0	4.5-4.6	Supergene
Native	Native antimony	Sb	94-98	6.65-6.75	Hypogene
Mercury ore	Livingstonite	HgSb_4S_7 ($\text{HgS} \cdot 2\text{Sb}_2\text{S}_3 \cdot \text{S}$)	53.0	4.81	Hypogene
Lead ore	Jamesonite	$\text{Pb}_3\text{Sb}_2\text{S}_6$	29.4	5.5-6.0	Hypogene
Copper ore	Tetrahedrite	$\text{Cu}_8\text{Sb}_2\text{S}_{13}$	24.7	4.4-5.1	Hypogene

Dry methods are generally adopted for the extraction of the metal. Electrometallurgical methods have had much attention in America and Germany and have not yet found, on economic grounds, practical or extended application, except in a few places. During recent years, treatment of the poor grades of the ore, especially sulphide, by ore-dressing methods, has commanded some attention and been adopted at a few plants.

The impure sulphide of antimony, resulting from the liquation process, is called "needle," "liquated" or "crude" anti-

needle antimony. Ores containing ± 50 per cent Sb are used in the liquation process for the production of crude. The temperature required for liquation is between 550° and 600°C . Ores to be liquated are broken to about walnut size. If the pieces are larger than this, the low heat used will not penetrate effectively, and if they are smaller the ore tends to pack too closely for adequate penetration. A packed charge also prevents the free escape of the fused sulphide.

Intermittent Liquation in Crucibles

The unique type of furnace that is in use in China for smelting is not highly efficient but is simple in construction and operation. The furnace is generally built

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in four sets of two pots each. The upper pot, which has a $\frac{1}{2}$ -in. hole at the bottom for the liquated product to trickle through, is the container, capable of holding a charge of from 45 to 60 catties (1.3 lb. each) and

ment of the residue by the volatilization process. It is regrettable that gas-firing has never been tried out, as it is obvious that by such a method a reducing atmosphere can be the better maintained.

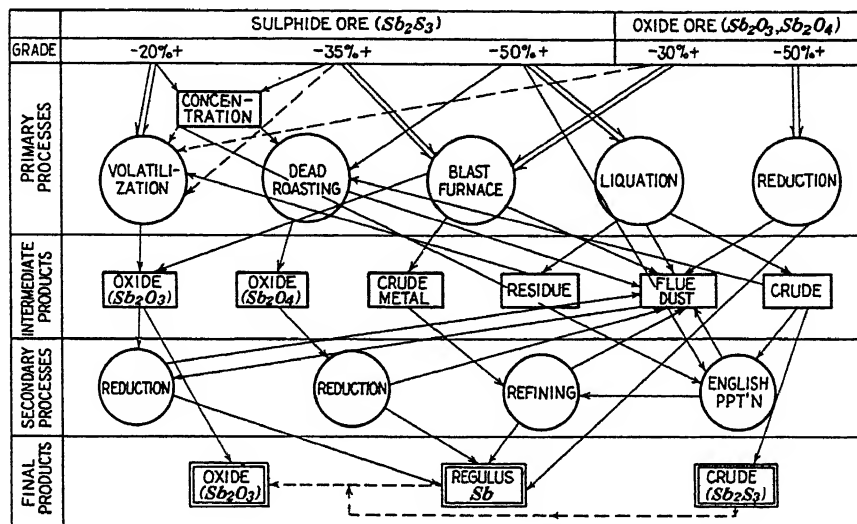


FIG. 1.—PROCESSES FOR TREATMENT OF ANTIMONY ORES.

the bottom pot, bedded in sand or ashes, is the receiver for the liquated product.

Continuous Liquation in Reverberatory Furnaces

The primary object of the liquation process is to free the sulphide of antimony from its associated gangue. As carried out in the old-fashioned pots, tubes, or crucibles, it is laborious, expensive and wasteful. On the other hand, although liquation can be easily carried out in reverberatory furnaces, the operation is attended with some difficulties. The maintenance of a reducing atmosphere, to prevent the formation of either the volatile trioxide or the stable tetroxide, is not easy to attain. While the trioxide can be partly recovered in any suitable flue or condensation apparatus, the tetroxide, which remains in the residue, has to be considered as a loss, since probably it can be recovered only in a very high temperature upon further treat-

The residue from the liquation process, generally retaining about 15 to 25 per cent Sb_2S_3 , may be treated in any of the volatilization furnaces to be described later.

ROASTING OF ANTIMONY ORES

Dead roasting as a process is seldom adopted, even with rich sulphide ore or crude, as there is no market for the intermediate product Sb_2O_4 and it must finally be reduced to the metal. Rich sulphide ores, containing ± 50 per cent Sb, are generally treated by the liquation process for the crude or by the English precipitation method for the metal.

The oxidizing roasting of antimony ore yields one of two products, depending on the temperature and air control—the volatile trioxide (Sb_2O_3) or the stable, nonvolatile tetroxide (Sb_2O_4).

When oxides of other metals are present, antimonates are formed. If, also, sulphides

of foreign metals are associated with the stibnite, these foreign metals are brought mostly to the form of antimoniates, instead of remaining, as they would under ordinary circumstances, as sulphates. If the proper temperature (below 500°C.) and an excess of air have been maintained, and if, in the case of rich ores, constant rabbling has been performed, the roasted mass should contain the tetroxide principally. Under ordinary working conditions, however, the product will contain antimony glass, undecomposed stibnite, and antimoniates, arsenates, and sulphates of the foreign metals present. Much attention must be paid to the regular rabbling of the charge as the richer parts of the ore tend to liquate and to frit together. The richer the ore, the more difficult it is to roast. Toward the end of the roasting, the temperature should be raised a little, in order to complete the oxidation of any undecomposed sulphide. If carried at too high a temperature, however, the mass will frit together, the penetration of air to the interior is prevented, and both the sulphide and oxide are volatilized.

A charge properly roasted is reddish in color while in the furnace, and ashy gray when cool, and there should be no evidence of fritting in the furnace. If an excess of air has not been available, the roasted product will be largely the volatile trioxide instead of the tetroxide.

VOLATILIZATION ROASTING FOR PREPARATION OF VOLATILE TRIOXIDE

Practically all of the shaft furnaces for the volatilization process are based on the same principle. The ideal ore for treatment in such furnaces is one containing antimony from 15 to 25 per cent; ore above 40 per cent Sb would partly volatilize and partly liquate, and part of the liquated product would combine with the volatilized trioxide to form an oxysulphide compound, commonly known as antimony glass, which causes fritting at the lower zone of the

furnace. Even with ore from 30 to 35 per cent Sb, some fritting might occur, necessitating the maintenance of a higher temperature than necessary for poorer ores. Hence the paradox: the richer the ore, the higher the percentage of coke required for the charge.

It is possible to volatilize an ore of about 20 per cent with 4 to 6 per cent charcoal, the temperature being thus kept at low red heat, but with liquation residue, which ranges from 15 to 25 per cent, the problem is different. This material disintegrates and packs at a very low red heat, thus partially blocking up the furnace and preventing free passage of the air upward. To remedy this, some works use a forced draft and others use an excess of coke, amounting to 30 to 50 per cent of the charge, thus increasing the porosity of the charge.

When the furnace is blocked, or when the suction fan is choked with the trioxide, especially if water is introduced into it, a reddish tint appears due to sulphide compounds of antimony in the trioxide fume issuing from the furnace. With the furnace working under normal conditions, this fume is white.

It is impossible to maintain uniform temperatures throughout the furnace shaft. The bottom part of the furnace, where the burned-out ore is ready to discharge, is cooled by the incoming air, while the top part is also comparatively cool. The central part thus localizes a hot zone of reaction where fusion of the silicate-forming minerals of the gangue and in the coke causes frequent trouble.

Otto Barth¹ says that the volatile trioxide exists only below 700° and above 1100° but our experience indicates that antimony sulphide, when roasted under properly restricted admission of air, changes to the volatile trioxide below 445° or 560° and above 930°, while between the two limits the oxide exists only as the stable

¹ References are at the end of the paper.

tetroxide. In practice, the stable tetroxide may be considered to exist between 500° and 1000° . It is thus obvious that proper control of temperature is important for the successful operation of the volatilization process.

for a number of years. There have been various modifications of it but the fundamental principles are the same. Its description here is not necessary, as it has been well described elsewhere.

*The Follisain Furnace.**—In 1926, Friedr.

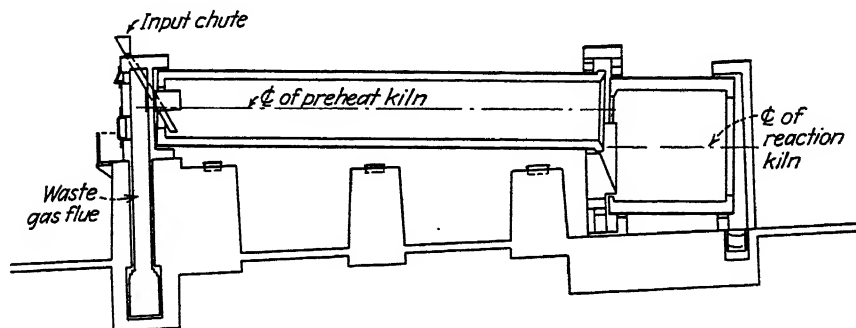


FIG. 2.—THE FOLLISAIN FURNACE.

The many advantages of this method of treating low-grade antimony ores have brought it into general favor and it is extensively used in one form or other in France, China, Yugoslavia and elsewhere. These advantages are:

1. When the ores contain* precious metals they are generally found in the residues after volatilization.
2. Barring dressing the ores, it is the only method really suited to low-grade ores.
3. With different devices for condensation, the loss of antimony can be greatly lessened.
4. Less fuel is required, as the sulphur in the ore can be utilized as fuel.
5. The condensed trioxide can be reduced to metallic antimony or it can be marketed as white oxide to make paint, enamels, and other products.

Modifications in Volatilization Method

Of the various modifications that have been developed in the volatilization method of producing antimony trioxide, the following important ones are described:

Herrenschmidt Process.—The Herrenschmidt process has been in use in China

Krupp-Grusonwerk A.-G. patented the so-called Waelz process for the treatment of zinc, lead, cadmium, arsenic, antimony, bismuth and tin ores. This process has been adopted by the Podringi Consolidated Mines Ltd., at its antimony-smelting work at Krupanj, Yugoslavia. In principle, the Waelz process is very similar to the Follisain process.

The Follisain furnace (Fig. 2) is a revolving furnace. The preheating kiln is approximately 30 ft. long and 36 in. internal diameter and the secondary or carbon combustion zone is about 7 or 8 ft. long by 6 or 7 ft. diameter. The air for combustion is heated in an air heater to about 750°C . The waste gases carrying the antimony trioxide fume leave the kiln at a temperature of 230° to 250°C . and enter a Cottrell electric precipitation plant for the recovery of the antimony trioxide.

Fuel consumption is from 25 to 30 per cent of the weight of ore charged. Power consumption is from $5\frac{1}{2}$ to 6 kw-hr. per ton of ore treated.

For the treatment of, say, 20 tons of 20 per cent Sb ore per day, two revolving

* Information from Follisain Syndicate Limited (London).

furnaces like the one illustrated are required.

*Smelter at Cortis Rosas (Ballao) Sardinia.*²—In the smelter at Cortis Rosas, a

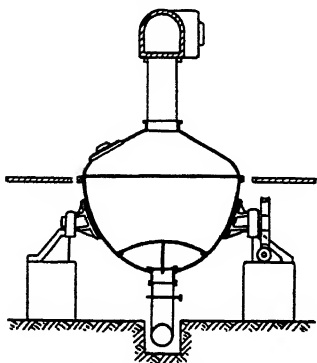


FIG. 3.—CONVERTER AT CORTIS ROSAS.

converter has been adopted for the volatilization process. It seems that this converter is an adaptation of the *convertisseur* apparatus patented by Collin³ in France.

The converter is composed of two parts, as shown in Fig. 3; the bottom part, which is hemispherical in shape and can be revolved horizontally on two bearings for the discharging of its contents, and the top part, which acts as a hood. Compressed air enters from the bottom while the volatile fume is drawn from the top of the hood by means of an aspirator. This method is especially adaptable to the treatment of fine ore, especially ore of a calcareous nature, which, if treated in a shaft furnace, would render the operation difficult and troublesome.

Other Processes.—There are perhaps a dozen processes for the preparation of the volatile trioxide, which at different periods in France, Italy, and Germany have had some prestige. In all of them, the principle of roasting, volatilizing, and condensation of the oxide is the same; differences exist merely in the forms of furnaces, condensers, and methods of collecting the oxide.

In the Chatillon process, which has been employed on a large scale in France, the

furnace consists of two double cupolas terminating in a common flue from which the volatilized oxides are led to water-cooled condensing chambers made of sheet iron. The upper cupolas are charged with alternate layers of fuel and ore, and as the liquated sulphide melts and falls through to the lower cupola it meets an upward current of hot air, which converts it into the trioxide (Sb_2O_3). Before leaving the plant the gases are reduced to a temperature of 100°C . and passed through a baghouse. The sublimate obtained contains 98 to 99 per cent antimony trioxide.

THE PIGMENTAL TRIOXIDE

The trioxide, as produced in the treatment of the ore by the volatilization process, is generally impure and coarse and hence is not suitable for pigmental purposes, although it may be used as an opacifying agent for white enamels.

The process adopted by the antimony smelter at Costerfield, Victoria, Australia, for the production of the pigmental trioxide was as follows:⁴

The furnace was a small circular cupola with four tuyeres at the top of the hearth and two more admitting air to the top of the charge above the feed door. The condensing section of this plant consisted of a firebrick and red brick chamber, a cyclone, and baghouse with a centrifugal fan placed in the circuit at the intake of the baghouse. The oxide with a small amount of reduction slag from the starring furnace was charged into the furnace on a bed of burning coke where it soon volatilized. The cooling of this oxide took place very rapidly so that it was deposited mostly in the amorphous form as very small spheres. A small amount of crystalline oxide was also collected at the cyclone. The bag-house product was the most suitable as a pigment on account of the fine state of division of the particles, approximately .0025 mm. in diameter, and its spherical form and whiteness.

Antonin Germot⁵ proposed to manufacture antimony trioxide by blowing air through a molten bath of metallic antimony and collecting the fume.

Jean Joseph Liatrat⁶ proposed to treat antimony sulphide ore, for liquation and volatilization as antimony trioxide, in one operation. However, it has been found in practice that antimony crude alone forms the best charge for such treatment. Air is blown through the molten antimony sulphide bath to form volatile antimony trioxide.

PRODUCTION OF METALLIC ANTIMONY

The last phase in the metallurgy of antimony is the production and refining of metallic antimony. Unrefined antimony metal is sometimes called crude antimony, but the metal is never marketed in this form; the name would be confused with liquated sulphide, which is commonly called crude antimony, or more correctly antimony crudum.

Antimony metal may be obtained from: (1) the oxides (trioxide or tetroxide); (2) from antimony crudum; or (3) by direct smelting of antimony ores. Up to the present time the bulk of the world's antimony has been produced by the first two mentioned, but in recent years the direct smelting of antimony ores has been done successfully in a number of places; for example, at the Laredo plant in Texas and at the Tlalapanltla plant near Mexico City.

The blast furnace is the best appliance for antimony ores containing from 25 to 40 per cent of metal. These are too high to be well suited for roasting, and are too poor for liquation or direct precipitation smelting. For these ores, as well as for by-products of the same richness, the blast furnace offers undoubtedly the best method of treatment.

Reduction of Oxide

Under the methods that have, in general, so far prevailed, reduction of the oxides is carried out either in reverberatory furnaces, in water-jacketed blast furnaces, or in crucibles.

In reducing the oxide, care must be taken to control volatilization and to keep any unaltered sulphide out of the mass of metal. In reverberatory melting, volatilization of metal is from 12 to 20 per cent and may be as high as 30 to 40 per cent with careless working. A fusible slag is utilized, which forms a cover to minimize volatilization, and which also dissolves any metallic sulphides left. This slag, composed of soda, potash, and Glauber salt, acts as a refining agent, carrying off most of the impurities that may be in the oxides.

In the Wah Chang antimony smelter, Changsha, China, the small reduction furnace can smelt two charges per 24 hr. of the following composition:

Sb ₂ O ₃	3000 lb. (1359 kg.)
Charcoal....	600 lb. (282 kg.)
Soda ash....	150 lb. (70.5 kg.)

The yield of regulus per 24 hr. from 6000 lb. (2718 kg.) of trioxide is from 4100 to 4300 lb. (1858 to 1950 kg.), which is about 70 per cent, exclusive of recoveries from furnace bottoms, flue dust and slag skimming, all of which may amount to at least 5 per cent of the regulus produced or 3.5 per cent of the trioxide. The consumption of coal is 0.55 ton per ton of regulus.

In some smelters, the furnace charge consists of about 500 lb. of roasted ore, oxidized ores, oxides, liquation residues, flue dust, etc., together with about 100 lb. of flux composed of salt, soda, about 70 lb. of ground charcoal, sometimes a small quantity of Glauber salt and slag from previous charges.

The flux is charged and melted first, and when all boiling or agitation of its surface has ceased the other materials are charged, about 40 lb. every 15 or 20 min. The charge is then well stirred, and the scum produced is drawn off. After the last charge, the temperature of the furnace is raised and kept up until the process is completed. The charcoal acts as a reducing agent, robbing the antimony of its oxygen, while

part of the soda combines with the sulphur and the remainder helps to slag off the gangue. Any other metals present are carried into the slag as sulphides by the action of the sulphide of soda produced through the reduction of the Glauber salt by the charcoal. Common salt serves the same purpose by carrying foreign metals into the slag as chlorides.

The fuel consumption is somewhere between 5 and 6 cwt. per charge and the loss usually is about 14 to 15 per cent. When considerable antimony sulphide is present, a little iron or iron slag may be added to assist in reducing the sulphide.

The charge is thoroughly rabbled after it has been about 6 hr. in the furnace, and the metal separates out from the slag. The slag is skimmed off and the metal is soon ready for tapping into molds. The "starring" of the regulus is done in the mold.

Extraction of Metal from Crude

Antimony crude or antimony "needle" is marketed and used for various purposes, such as vulcanizing rubber, match making, and ammunition manufacture, but the quantity required for these purposes is limited, therefore it is necessary to convert the greater part of it into antimony regulus. This may be done in one of two ways: (1) conversion of the sulphide into antimony oxides, and then reduction of the oxides in reverberatory furnaces; (2) direct smelting of the sulphide to metal, iron being added as the reducing agent.

In China, the English precipitation method has been found too inconvenient and costly to compete successfully with the oxidizing methods, and the latter have become the accepted mode of treatment for crude in that field. In England, Hungary, Japan, and Mexico, however, the precipitation method remains in vogue, rich ore or antimony crudum being directly reduced to metal by crucible fusion with metallic iron.

The fundamental principle involved in the English precipitation method is the greater affinity of sulphur for iron than for antimony. As this method has been adequately described elsewhere, it is not necessary to repeat it here.

Several patents have been taken out (Sanderson, Cookson, Herrenschildt) on the direct smelting of antimony sulphide in a bath of ferrous sulphide, on the hearth of a reverberatory furnace. This method has given good results, but has had no wide adoption commercially. After the hot ore has been charged into the reverberatory and thoroughly rabbled, iron is added, together with a certain amount of soda ash, the temperature raised, and, when decomposition of stibnite by iron is complete, the antimony metal is tapped. The taphole is closed as soon as the iron sulphide appears; slag is drawn through the working doors, and as the iron sulphide increases during the operation it is removed until the bath is reduced to its original depth.

Smelting in Water-jacketed Blast Furnace

The blast-furnace smelting of antimony ores, both sulphide and oxide, is entirely feasible, and undoubtedly will come into more common use as the industry advances. In Mexico, California, and England, successful blast-furnace smelting has been under way for several years, proceeding along lines only slightly modified from regular lead-smelting practice. That the antimony blast furnace will extensively replace the old existing methods in Europe, Mexico, and America there is little question but under existing ownerships and conditions in China it is improbable that any reshaping of the industry will take place there.

Sulphides.—Attempts to smelt unroasted stibnite ores in water-jacketed blast furnaces were not successful until very recently, and published information on the subject is exceedingly meager.

There is a marked difference in the behavior of stibnite and that of other metallic sulphides in the blast furnace. It has been found best to add no metallic iron on the charge, and to regulate the coke so as to preclude any reduction of ferrous oxide in the flux. No iron available for matte is provided, and matte is usually absent. Any addition, or presence, of metallic iron will always result in the production of an antimony-iron alloy—i.e., speiss.

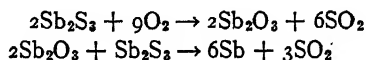
Usually the contents of the furnace crucible freeze gradually from the bottom upward, and the entire crucible is eventually a solid mass. Frequently the crucible is filled with firebrick, and the mixed flow of slag and metal is separated in a shallow reverberatory forehearth.

While the blast-furnace smelting of stibnite has not enjoyed the long industrial history of the volatilization and English precipitation methods, it is to be stated that the best conditions for the process appear to be: less than 10 per cent of coke, low blast pressure, low metal content of the charge (about 10 per cent), high smelting column (over 15 ft.), and separation of slag and metal in a heated forehearth. In an efficient plant, the great bulk of the volatilized material is recovered in bag-houses, but it is, of course, undesirable to have to re-treat a large amount of fine material unsuitable for blast-furnace work. The flue dust is best treated in a reverberatory, while the fume is useful in refining, or it may be used as raw material for the manufacture of antimony compounds.

The blast-furnace process does not appear to be adapted for the treatment of high-grade stibnite ore. Loss by volatilization is common to all forms of antimony smelting, and in this respect the blast furnace is far worse than the reverberatory, where a layer of flux or slag protects the metal. With low-grade material, however, which it is difficult or wasteful to treat by other methods, the blast furnace offers

decided advantages; i.e., where large quantities of poor ores, foul slags, mattes, or liquation residues must be worked up. It is a favored mode of smelting for all materials containing from 25 to 40 per cent Sb, which can be mixed with fluxes to give a charge sufficiently poor in metal to hold down volatilization.

It is pointed out by Schoeller⁷ that the production of antimony from stibnite in the blast furnace is an oxidizing process in which the metal is formed in two stages that proceed simultaneously: first, the molten stibnite absorbs oxygen from the blast; secondly, the oxide at once reacts with the unaltered sulphide (roast-reaction process) to form metal and sulphur dioxide, thus:



In endorsing this theory, it is realized that it has been a commonly held belief that antimony sulphide and trioxide do not react on each other as do the corresponding lead and copper compounds, but that the antimony compounds fuse together to an antimony glass. The latter reaction occurs, without question, if the oxide-sulphide mixture is fused in a crucible under a layer of salt, but if stibnite is roasted with insufficient access of air, some oxide will be formed, which will react with the unaltered sulphide and part of the antimony will settle out in a metallic state. The roast-reaction process, therefore, does have a part in the smelting of antimony.

Oxides.—Roasted ore, briquetted flue dust and oxides, and smaller amounts of unroasted stibnite, together with siliceous waste for slag-forming material, make up the charge. Recovery of antimony runs 95 to 98 per cent, slags carrying about 1 per cent, sometimes as low as 0.25 per cent, of antimony.

The Cookson plant, at Wadley, Mexico, handled ores of a refractory nature and of comparatively low grade. The antimony

content varied from 25 to 40 per cent. The ores at Wadley, in the main, were oxidized, between 80 and 90 per cent of the antimony being present as oxide. The gangue was siliceous and calcareous. On account of the refractory nature of the ores and their oxidized condition, Mexican utilization of the comparatively simple methods of smelting adopted in China was not satisfactory, nor could the usual English methods be employed. They have, however, proved amenable to blast-furnace treatment. The Wadley plant was seldom in operation with antimony below 12 cents per pound, c.i.f. New York.

The ores, after rough concentration, were smelted in rectangular water-jacketed blast furnaces, with limestone and iron ore as fluxes and coke as reducing agent. The furnaces were some 28 ft. high with 5 by 3-ft. hearth area, and were blown by compressors delivering air at a pressure of from 2 to 3 in. of mercury. A forehearth separated the metal from the slag.

Owing to the high temperature attained in the blast furnace, and to the volatility of antimony, efficient baghouses were necessary to deal with the fume carried over in the gases. The briquetted fume was recharged to the blast furnaces.

*The Mace Blast Furnace.**—The Mace blast furnace is a distinct improvement on the usual type of blast furnace for antimony smelting. The main variations from the old type of blast furnace are: (1) diametrically opposed rectangular tuyeres below the shaft of the furnace instead of the circular tuyeres spaced at regular intervals in the lower part of the water jackets, and (2) a removable crucible instead of a solid crucible built on the ground. There are several advantages in the use of the rectangular tuyeres, which extend the full length of the furnace on both sides. The whole hearth area is active and the dead spaces between the tuyeres of the older types of furnaces are eliminated. This gives

a uniform and intense combustion over the entire hearth.

On account of the open tuyere, the Mace furnace uses lower blast pressure (as low as 4 oz. per sq. in.), which is an important feature in continuous operation of the smaller units. The tuyeres are so constructed that the opening into the furnace hearth can be adjusted. For oxidation and volatilization smelting, the slot is left wide open, so that a large volume of air under low pressure can be admitted. For reduction smelting, the slot is narrowed. Another advantage of the open tuyere is that any accretions can be removed from the furnace by drawing them into the windbox with the hook instead of punching the dead material back into the furnace, as is necessary with the circular tuyeres. The advantages of the removable crucible are evident.

The antimony plant set up in 1942 at Tlalapantla, near Mexico City, has a Mace furnace in operation. Oxide ore containing a small amount of stibnite and some livingstonite is treated. The gangue is principally silica, running from 45 to 52 per cent, and the antimony on charge is 35 to 38 per cent. Limestone and hematite are used for flux to slag the silica, and the furnace charge is about 50 per cent ore, 50 per cent flux, with 15 per cent of the weight of the charge coke. The low column and hot top volatilize a maximum amount of the antimony. A small amount of antimony single metal, assaying 91 per cent antimony and 9 per cent iron, is produced, but no matte. The baghouse oxide assays 81.6 per cent antimony and apparently the only impurity in it is a small amount of carbon dust from the coke. The material is mixed with 15 per cent fine charcoal and 6 per cent soda ash and reduced in a reverberatory furnace to metal. The capacity of the furnace is 30 tons of charge in 24 hours.

Hodson-Wang Process of Antimony Smelting

An interesting combination of accepted methods of ore reduction is found in the

* Communication from H. C. Mace.

Hodson-Wang-Hodson continuous "flash" process,⁸ which utilizes the heat of the reduction reaction and also permits removal of all gangue from the ore during roasting treatment. Pulverized ore is generally used, although one adaptation of the process is designed for use of lump ore.

The crude ore is roasted in an externally heated vertical or horizontal chamber by waste gases from the reduction furnace. Antimony in the ore is carried off to the main reduction chamber as trioxide gas and all gangue matter drops to the bottom of the first chamber. The volatile trioxide formed is injected directly into a vertical shaft furnace with a gaseous medium (or with preheated air and carbon) and the mixture of reducing gas and oxide particles is kept in violently turbulent motion by a sudden reversal of direction. This agitation in the reducing gas promotes speed of reaction and prevents formation of an envelope of nonreducing gas around the oxide particles. The reduced metal, in fine liquid form, is collected in a lower chamber. With arsenical ores, usually sulphide, the arsenic forms volatile arsenic trioxide in the first (roasting) chamber together with the antimony trioxide. It is reduced along with antimony in the second chamber. However, as arsenic sublimes at a temperature of 615°C., and the reduction furnace is kept at about 800°, the antimony condenses out as a liquid, while arsenic remains a vapor and can be carried off with the gases for subsequent collection.

BY-PRODUCTS OF ANTIMONY SMELTING

The by-products produced in the procedures described include liquation residues, matte, slags, and flue dust. The slags obtained from the extraction by the roasting and reduction method consist principally of silicates; those from the precipitation method, silicates and sulphides. They are thrown away if not sufficiently rich to be used in the first smelting

of the ores. The other by-products are all added to the charges in smelting the ores, the liquation dross being first roasted. The flue dust is intimately mixed with soda ash before smelting. Liquation residues are also sometimes treated separately in shaft furnaces.

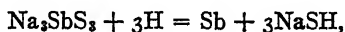
EXTRACTION BY WET METHODS

Extraction of antimony from its ores by wet methods has had much attention in European centers, but it is still a matter there of academic discussion rather than practical application. Solution of stibnite is readily effected in sodium sulphide, sodium hydroxide, or calcium sulphide, and from such solutions antimony sulphide is precipitated by carbon dioxide or sulphurous acid.

In the past, poor antimony ores either have not been used or have been subjected to a volatilizing roast, with subsequent reduction of the trioxide. This is, however, a somewhat laborious metallurgical operation, and the application of electrolytic methods as a means of extraction from poor ores has long been desired.

During the high-price years, a small amount was produced by electrolytic methods, the solvent being a 6 per cent sodium hydroxide solution, which gives an extraction without serious contamination by other metals. This solution, electrolyzed, deposits antimony of a very high purity, but in ordinary times the deposition of the antimony and the necessary regeneration of the electrolyte are too costly to make the process commercial. The chief difficulty is a troublesome accumulation of thiosulphate at the anode.

When the solution is electrolyzed, the reaction at the cathode seems to be:



while at the anode sodium thiosulphate and Na_2S_2 are formed by oxidation. The 6 per cent NaOH solution holds about 3 per cent of antimony at first, but as

thiosulphate accumulates the solvent power decreases until there has accumulated one atom of sulphur for each atom of sodium present; by this time the solvent power has dropped to about 0.7 per cent. When this amount of sulphur has gone into solution, the iron anode begins to corrode, and falls to pieces rapidly. A practical, insoluble anode has not been found.

The continuance of the process beyond this point, at which the sulphur in solution begins to be in larger atomic percentage than the sodium, requires the regeneration of the solution, or the furnishing of a new one. If a new solution is applied, it means the consumption of one pound of NaOH per pound of antimony.

One way of handling this situation has been proposed by Demorest, which contemplates evaporation of the solution to dryness with exhaust steam; roasting the residue in a reverberatory furnace to get rid of about half of the sulphur, thus changing the thiosulphate to sulphate; then mixing with coal and heating until it has all been reduced to Na_2S , which quickly dissolves stibnite and can be put into the circuit again. Small-scale experiment shows this to be successful, but it has not been tried on a large scale.

Sunshine Mine, Idaho.—In September 1942, commercial electrolytic production of antimony from an argentiferous tetrahedrite (a silver-copper-antimony sulphide) was inaugurated by the Sunshine Mining Co. at Kellogg, Idaho.⁹ A solution of barium sulphide is here employed satisfactorily as a regenerating agent. The barium sulphide not only regenerates the oxidized sodium salts back to the effective Na_2S solvent but also gives a precipitated barium-sulphur-oxygen salt that can be reduced back to barium sulphide for re-use in the regenerating circuit. Briefly, the Sunshine process is as follows:

1. The tetrahedrite concentrate produced in the mill is batch-leached in hot concentrated sodium sulphide solution.

2. At the completion of the leach cycle, the pregnant solution is separated by settling and decantation. The residue is recovered by a double filtration with a repulping step between stages.

3. The pregnant solution is electrolyzed in batches in banks of diaphragm cells, recovering the antimony on mild-steel cathodes.

4. The fouled solutions from the cell bank, both catholyte and anolyte, go to the regeneration circuit for treatment with the required amount of barium sulphide (BaS) solution.

5. After separation from the precipitated barium salts, the solutions are ready for re-use in the leaching circuit.

6. The precipitated salts from step 5 are mixed with coal and passed through a rotary kiln for reduction to a black ash containing barium sulphide.

The process is cyclic and regenerative except that some barite must be added to the kiln circuit to meet the barium sulphide requirements, and some caustic soda added to the anolyte circuit to make up for the sodium lost in the copper residue shipped to the copper smelter.

Yellow Pine Mine, Idaho.—J. Koster and M. B. Royer¹⁰ have developed a process for the treatment of antimonial gold concentrates from ores found in the Yellow Pine mine at Stibnite, Idaho, of the following composition: Au, 1.66 oz. per ton; Ag, 6.34 oz. per ton; Sb, 15.6 per cent; As, 5.5; Fe, 19.1; S, 25.0. The process includes electrolytic refining of impure antimony metal, using a fluoride sulphate electrolyte.

Bunker Hill and Sullivan, Idaho.—At the Bunker Hill and Sullivan Mining and Concentrating Co., Kellogg, Idaho,¹¹ tetrahedrite ($3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$) concentrates mixed with Na_2CO_3 , Na_2SO_4 and coal are fed to a three-electrode electric furnace. Current at 50 to 110 volts, flowing from electrode to furnace wall, the charge serving as the resistance, yields a melt temperature of about 2300°F. Matte is tapped from the furnace, cooled and crushed to pass 80 mesh. The ground matte is leached with water at 140°F. to form the electrolyte.

Undissolved pulp is crushed and tabled to yield a concentrate of Sb-Bi-Ag alloy and a tailing containing 25 to 30 per cent Cu and 1 per cent Sb, the latter being added to the copper smelter charge. From the electrolyte containing the thioantimonate (Na_2SbS_4) Sb is deposited upon sheet-steel cathodes. The anodes are sheet lead.

There is no material corrosion of either electrode at operating current density of 20 amp. per sq. ft. Cathodes are stripped of their antimony every 6 days. Spent electrolyte containing about 2 to 5 grams per liter is recycled to the leaching tanks. The antimony, being brittle, is easily removed from the cathodes. This plant, erected at a cost of about \$500,000, started operations in March 1940.

REFINING OF ANTIMONY METAL

Unrefined antimony usually contains sulphur, iron, arsenic and copper, and lead. These impurities, except lead, can be eliminated partly by oxidizing and slagging agents, partly by sulphurizing agents, and partly by chlorinating agents.

Soda or potash or antimony glass (antimony oxysulphide) removes sulphur by fusion and converts arsenic into arsenate of soda or potash. The conversion of copper and iron into their sulphides by sulphide of antimony can be facilitated by the addition of soda or potash, or of Glauber salt and charcoal. These sulphides form a slag with the sulphide of sodium produced from the reduction of the Glauber salt, and with the soda or potash present. The sulphides are easily removed by antimony glass.

The use of common salt, carnallite, or magnesium chloride to volatilize some of the foreign metals present as chlorides and to slag others may occasion great loss of metal due to volatilization. It is somewhat difficult to remove the lead, and when antimony ores are found to contain a considerable percentage of lead, as they

often do, they may with advantage be smelted together with lead ores to produce hard, antimonial lead (12 to 15 per cent Sb).

One of the most objectionable impurities found in antimony is arsenic, because great loss of the metal and expense are entailed in trying to bring the arsenic down to the market tolerance. Obviously, the best way to obviate this difficulty is to free it as much as possible from the ore before it is smelted. This can be done by differential flotation of the arsenic mineral, or, as suggested by Koster and Royer,¹⁰ by roasting the ground ore or concentrate at 475° to 500°C. with steam at atmospheric pressure. In the treatment with steam, approximately 88 per cent of the original arsenic will volatilize off, and the loss of antimony will be only 10 to 15 per cent.

Arsenic in antimony regulus may be reduced by blowing air through the molten metal. Merson, Krol and Krein¹² recommend the following optimum conditions for carrying out a refining treatment to bring the arsenic content in the metal down to 0.05 per cent:

1. Temperature, 950°C.
2. Air supply, 500 ml. per min. per kg. of metal.
3. Amount of soda slag, 20 per cent; the slag being renewed once during refining.
4. Duration of refining, 1 hr. under each slag; total, 2 hours.

Under these conditions a yield of 89.5 per cent of refined antimony was obtained; 8.75 per cent passed into the slag while 1.75 per cent volatilized off as Sb_2O_3 .

Another method of refining antimony containing appreciable amounts of arsenic is to melt the metal, which is crushed to from 10 to 15 mesh, with about 5 per cent of niter and the same amount of soda ash.

Starring

It has long been the practice of the trade to judge the purity of refined anti-

mony by the development of a fernlike structure, or "stars," on the surface of the ingot. The appearance of this structure does not actually indicate the relative purity of the metal, but is only the result of cooling it slowly under cover of a layer of a properly prepared starring mixture—couverture—a slag that has a fusion point lower than that of antimony, which is 630°C .

When the regulus contains impurities like sulphur, arsenic, lead, or iron to any appreciable extent, its surface shows the presence of these foreign elements by specks, by a leaden appearance, or by a poorly defined appearance of the fernlike structure. It is true, on the other hand, that regulus containing impurities above what are considered to be the limits imposed by the market, often shows stars as bright and well defined as those of well-refined regulus.

restarting the star bowls, also a pot-furnace operation, is as follows: The lumps of metal, when cold, are removed from the mold and are thoroughly cleaned from the adhering skin of slag by chipping with sharp hammers, this part of the work being sometimes done by women. The chippings are returned to the second smelting. Having been cleaned, the star bowls are broken small. The charge made is about 84 lb., together with enough flux to surround the ingots completely; the quantity generally is 8 lb. for ingots of the ordinary shape.

The metal is charged first and is closely watched; as soon as it begins to melt, the flux is added; and as soon as the fusion appears to be complete the furnaceman stirs the mixture once round only, with an iron rod, and the charge is then poured. The ingot must be completely surrounded by the flux; there must be a thin layer of

TABLE 2.—*Couverture Mixtures*

Crude (High-grade)		Antimony Tetroxide (Well-roasted Crude), Sb_2O_4	Antimony Trioxide, Sb_2O_3	Potash, K_2CO_3	Soda ash, Na_2CO_3	Charcoal, C	Smelters Using the Mixtures
No.	Sb_2S_3 , Per Cent						
I	15	24		10	1	1.25	Pao Tai
II	15	24		11	3	1.25	Pao Tai
III	2.2	13.2		7.5		5.7	Tao-chang
IV	4.5		20		5	0.5	Loong Kee
V	7		18		4	0.5	Tai Wo
VI	3-4		32		2-4	1	
VII	5	30			5-6	1	Pao Tai
VIII			85		15		Wah Chang
IX			4-5	1-2.5			Wah Chang
X			8	1			
XI			40	1	4		
XII			7		1		Loong Kee
XIII	6		16*		1	0.5	Pao Tai
XIV	7	14			0.5	0.5	Pao Tai

* Pure flue dust.

Since buyers demand this artificial adornment on the regulus, the starring operation has become a regular part of the refining process, adding an unnecessary cost of from \$5 to \$30 per ton.

Different mixtures for this couverture are shown in Table 2 as used, according to local conditions, by various antimony smelters in China.

In England the process of refining and

flux between the mold and the metal, and the whole surface of the ingot must be covered by the flux to a depth of $\frac{1}{4}$ inch.

The flux is used over and over again, being regenerated by the addition of carbonate of potash.

Refining in Small Reverberatory Furnaces

In small reverberatories, 1200 to 1500 lb. of impure antimony is melted as one

charge, to which is added 3 to 7 per cent of soda, mixed with a little coke dust or fine charcoal. The slag from this fusion gradually becomes thicker, and after about 3 hr. is skimmed off through the working door. The iron and sulphur remaining in the metal are next removed by addition of ingredients capable of forming antimony glass, such as oxysulphide of antimony. For each 100 lb. of antimony in the charge, 3 lb. of liquated sulphide of antimony and $1\frac{1}{2}$ lb. of antimony tetroxide are thrown in, and as soon as these are fused, $4\frac{1}{2}$ lb. of potash is added. The bath of metal must be completely covered with the fluxes.

The metal can be ladled out after another 15 min., but must be handled cautiously in order to secure the starred appearance of the ingots.

Three charges of about 1500 lb. each can be refined in 24 hr. in one of the small furnaces used, with a coal consumption of 1300 pounds.

The slag obtained in the final step of the refining operation is called "star slag," it consists principally of antimony glass, carrying from 20 to 60 per cent of antimony. It is used repeatedly for refining, until it becomes too impure for the purpose, when it is charged with the ore for the first smelting. The other slags obtained in the course of refining are also added to the smelting ore charges.

The proper procedure for charging any of the mixtures is as follows: The compound, after being thoroughly mixed, is immediately charged into the reduction furnace as soon as the skimming is finished. The doors are closed and vigorous firing is maintained. As soon as it is observed that the mixture is completely melted, ladling commences. Each ladle dips into the molten metal and, in coming out, picks up a certain quantity of the molten couverture, which, when poured out together with the metal into a hold mold, completely covers the metal on all sides. Ladling must

be done rapidly for each moldful—four or five ladles to one slab of regulus, according to the size of the ladle used. The thickness of the solidified couverture varies from 1 to 2 mm. on all sides except the top, which varies from 5 to 7 mm. The amount of couverture required for each charge varies from one sixth to one fourth the weight of the regulus produced.

SUMMARY

The sulphide ore, stibnite, is the only ore of practical importance; the oxide ores (valentinite, senarmonite or cervantite) being of minor significance. Beneficiation of low-grade ores by gravity concentration, air concentration and flotation is under way and/or planned in all the producing regions where freight to distant smelting points must be considered or where the ore contains valuable constituents other than antimony.

For an ore containing an appreciable amount of arsenopyrite, it is sometimes advisable to use differential flotation to get rid of the arsenopyrite, which otherwise would contaminate the product from the pyrometallurgical treatment of such ore. Of all the concentration methods, flotation appears to be by far the most satisfactory.

Hydrometallurgical or electrolytic methods of extracting antimony are uneconomical, and only under exceptionally high prices and special circumstances may their adoption be recommended.

It is to be emphasized that, whatever smelting method is followed, an antimony plant must have a particularly good flue and condensing system. With ordinary settling devices—such as flues with reduction or expansion of cross sections, Freudenberg plates or Roesing wires—only dusts larger than 10 microns (10^{-3} cm.) can be deposited, hence antimony fumes, in which the particles range from 0.3 to 1.0 micron, and settle very slowly even in still air, cannot be effectively deposited. The usual cyclone dust catcher acts

ineffectively with antimony fumes; even the multiclone¹³ cannot settle particles smaller than 5 microns. Filtration of antimony fumes by means of bag filters, woolen or cotton, has been adopted at many antimony works.

The Cottrell process of electrical precipitation has been adopted at a few places and has proved its worth as a secondary cleaner for the oxide fumes.

The scrubbing or washing of antimony fumes, involving as it does the intimate mingling of the fumes by means of sprays or jets of water, is not thoroughly effective in precipitating the oxide. However, the Peabody process,¹⁴ as recently developed in England, is an improvement of the old-time scrubber and may be applicable to the condensation of antimony fumes.

For different grades of ore, the following methods are generally adopted:

1. For sulphide ore containing ± 20 (approx. 15 to 25) per cent Sb, the volatilization method.
2. For sulphide ore containing ± 35 . (approx. 25 to 45) per cent Sb, the blast-furnace method.
3. For sulphide ore containing ± 50 (approx. 45 to 60) per cent Sb, the liquation method, and the English precipitation method.
4. For oxide ore containing ± 30 (approx. 25 to 40) per cent Sb, the blast-furnace method.
5. For oxide ore containing ± 50 per cent Sb, the direct reduction method.
6. For mixture of sulphide and oxide ore, the blast-furnace method.

Dead roasting of sulphide ore to the stable tetroxide, as a process for the treatment of rich ore, has become obsolete.

PRODUCTION ECONOMICS

The average yearly world production of antimony, including crude and oxide in antimony content, during the period from 1908 to 1938 was about 27,700 metric tons.

Of this, China furnished 62 per cent, Mexico and Bolivia, each about 11 per cent, totaling about 84 per cent of the world production. The remaining 16 per cent was supplied by the United States, Algeria, France, Czechoslovakia, Italy, Yugoslavia, Peru and Argentina, with insignificant outputs from other countries.

Increased demand, war-born, for strategic metals has been coincident with global shifting in sources of raw material. For no commodity has the supply picture shifted more extensively than for antimony. In comparison with the normal movement of 65 to 70 per cent of world supply from China and 30 to 35 per cent from other sources in the eight years prior to the Japanese-Chinese war, the years 1942 and 1943 were drawing approximately 49 per cent of world production of new metal from Mexico, 35 per cent from Bolivia and Peru, 14 per cent from the United States, 2 per cent from various other regions. This was a forced draft on many of these areas, and it is believed probable that postwar economics will turn the searchlight back to the preponderant Chinese supply.

Though actual Chinese export to the United Nations has dwindled to almost nothing, production in the Asiatic fields has continued in varying degrees as a matter of national economy and human livelihood, and Chinese stock piles of antimony—ore and metal, exact quantities unknown—are accumulating as a cushion for such postwar raw-material exhaustion as may develop.

Return of commodity normalcy, postwar, is expected to register, in the antimony industry: (1) 25 per cent shrinkage, by and large, of current world demand; (2) inability of Western Hemisphere areas, recently prolific, to maintain preponderance of supply; (3) reversion to Asiatic supply area.

Under normal conditions the relatively high cost of production in the United States due to wages for labor and mining

costs prevents successful competition with Chinese metal.

The antimony-producing countries of the world may be divided into three groups:

1. Principal potential production, in order of importance: China, Mexico, Bolivia.

2. Irregular in normal times but with potential reserves available at higher price levels: United States, Yugoslavia, Peru, Czechoslovakia, Algeria, Italy, Australia, French and Spanish Morocco, Canada, Turkey (Asia Minor).

3. Production small, known reserves probably less important: Hungary, Russia, Argentina, Portugal, Burma, Indo China, British India, Japan, Southern Rhodesia, South Africa, Borneo, Greece.

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Beryllium

BY DONALD M. LIDDELL,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1944)

FROM a commercial standpoint, the only beryllium mineral warranting attention is beryl, $3\text{Be} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, which is of fairly widespread occurrence. The chief deposits are in Brazil, Argentina, India, Canada and Portugal. When pure this contains about 14 per cent of beryllium oxide. The mineral richest in beryllium is phenacite, $(\text{BeO})_2\text{SiO}_2$, or beryllium orthosilicate, which contains 45.55 per cent beryllium oxide when pure, and if anyone is ever fortunate enough to discover a large deposit of it, it will revolutionize beryllium metallurgy.

Gadolinite, $2\text{BeO} \cdot \text{FeO} \cdot 2\text{Y}_2\text{O}_3 \cdot 2\text{SiO}_2$, is also often referred to as a beryllium mineral, though the occurrences are comparatively scant and it is of more interest as a source of yttrium than it is of beryllium.

There has been a good deal of talk recently regarding some occurrences of helvite in the United States. Helvite is a complex manganese-iron beryllium silicate and, apart from difficulties that would arise in its treatment because of its composition, the beryllium content of the known deposits is not high.

EARLY METALLURGY

The element beryllium was first isolated by L. N. Vauquelin in 1797.¹ He crushed and heated beryl, having the idea that

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¹ *Ann. de Chimie et de Physique* (1798) 26, 115-179.

this heating made it more readily amenable to attack by chemicals, and then mixed the mineral with three times its weight of caustic potash and fused the mixture. The melt after cooling was dissolved in hydrochloric acid, dehydrated, and again taken up with hydrochloric acid and filtered to separate the silica. The filtrate was treated with an excess of potassium carbonate and the precipitate after draining was leached with a solution of caustic potash, which dissolved the alumina. The undissolved material was, in Vauquelin's own words, "une terre nouvelle."

He dissolved the precipitate with nitric acid and evaporated it to dryness, took up with hydrochloric acid and threw the iron out with potassium hydrosulphide, though he found that to make a complete separation of the iron involved a second treatment. The solution, after throwing out of the iron, had a pronounced sweet taste, and though Vauquelin always speaks of working on "terre du beril" he suggests that the new element should be known as "glucine" (glucinum) from the Greek word for sweet, because of this outstanding property.

Vauquelin did considerable work on the comparison of aluminum and beryllium, working out a separation of most of the aluminum based on its precipitation as alum. His work is reviewed at some length, since ordinarily his procedure is incorrectly stated. It will also be recognized by those who have studied beryllium metallurgy that a good many technicians have followed his ideas since, including preheating the beryl before treatment. The fusion with

caustic alkali has been done by H. N. Warren (1894), G. Wyruboff (1902), J. H. Pollok (1903), C. L. Parsons and Barnes (1906), F. Bran and G. Van Ordt (1907), L. Petit-Devaucelle (1926), and C. F. Brush, H. Fischer, H. H. Armstrong, E. Jaeger and C. Adamoli, to cite only those processes immediately occurring to the author. R. H. McKee worked with alkalis in solution in an autoclave, rather than by fusion.

Vauquelin also proved the existence in the emerald of the same new element he had found in beryl.

Humphrey Davy (about 1808) and Wöhler (1827) produced an impure metallic beryllium by reducing the oxide with metallic sodium or metallic potassium.

Henri Debray in 1854 pulverized beryl and fused it with half its weight of calcium oxide.² The mass obtained by this fusion he powdered and treated with dilute nitric acid until a homogeneous jelly was produced. Then he evaporated to dryness and calcined until the nitrates of beryllium and iron were decomposed as well as some of the calcium nitrate. This residue he treated with ammonium chloride. Apparently he counted upon the evolution of ammonia by the decomposed calcium nitrate to keep most of the iron and alumina in the insoluble residue with the silica. If there was no evolution of ammonia he argued that he had not carried his calcination far enough. He filtered off the solution of beryllium and calcium and poured the filtrate into an excess of ammoniacal ammonium-carbonate solution and allowed the mixture to stand for seven or eight days, then added some ammonium hydrosulphide to precipitate the iron completely. He then filtered off the pure beryllium solution which he concentrated by boiling until basic beryllium carbonate separated as a white powder. Again metallurgists who have worked with beryllium

will recognize that Debray's caustic lime decomposition of beryl has formed the basis for at least a dozen metallurgical processes based on this method of attack.

Debray refers at some length to Berthier's work on the separation of beryllium from alumina. Berthier suspended the well washed mixture of these earths in water and passed in sulphur dioxide until they dissolved, after which he boiled off the excess of sulphur dioxide. Berthier claimed that the alumina precipitated and left the beryllium in solution. Debray thinks it is an inferior separation, although it still figures in some modern patent work.

The first decomposition of beryl with fluorine that the author has found was that of G. Scheffer in 1858, who treated beryl with fluorspar and sulphuric acid, driving off the silicon as silicon tetrafluoride.³ The excess hydrofluoric acid was also driven off. He leached the residue with dilute sulphuric acid and threw out most of the alumina as an ammonium or sodium alum. The rest of the alumina was thrown out by treating the solution with zinc, which produced an insoluble basic aluminum carbonate. The zinc then had to be removed in part as potassium-zinc sulphate and finally as zinc sulphide, the beryllium eventually being precipitated by the use of ammonium carbonate.

John Gibson, in 1893, decomposed beryl with ammonium fluoride. This will also be recognized as a precursor of various recent patents. P. Lebeau, as early as 1895, described a process based on fusing beryl with twice its weight of calcium fluoride, which he stated could be done at a comparatively moderate temperature. He treated the melt with sulphuric acid, driving off silicon tetrafluoride and hydrofluoric acid.

Lebeau also treated beryl in an electric furnace with an excess of carbon, reducing some of the silica to silicon, which distilled

² *Ann. de Chimie et de Physique* (1855), 54, 3rd Series, 5-41.

³ *Ann. der Chemie und Pharmacie* (1859), 33, 144-147.

off, and in part reducing it to silicon carbide and ferrosilicon. The aluminum and beryllium were converted into carbides. This electric-furnace product disintegrates by weathering and is easily attacked by sulphuric acid.

ELECTRIC FURNACE PROCESSES

Other metallurgists also worked with the electric furnace. L. Burgess produced beryllium carbide or beryllium silicide in an electric furnace, distilling off beryllium chloride. He reduced under such conditions as to form tetraberyllium trisilicide and also worked on a method for concentrating beryllium in a scoria by forming ferrosilicon in the furnace, using an insufficient amount of carbon to reduce the beryllium (U. S. Patent No. 1905340 of 1933).

B. R. F. Kjillgren also worked on this idea of the production of ferrosilicon (U. S. Patent No. 2092621 of 1937).

H. Lowenstein based his process on the production of beryllium sulphide, using pyrite as a source of his sulphur and thus sulphurizing the beryllium (U. S. Patent No. 1777267 of 1930).

D. Gardner worked on the production of beryllium sulphide by sulphurizing with carbon disulphide in the presence of an excess of carbon at 1800° to 2000° (U. S. Patent No. 2166659 of 1930).

H. H. Armstrong reduced with carbon or CaC_2 at a temperature high enough to volatilize the silicon, then leached with H_2SO_4 (U. S. Patent No. 2273168 of 1943).

REDUCTION TO METAL

Although certain early experimenters, following the procedure of Davy and Wöhler, claimed to have produced beryllium 99.8 per cent pure it seems probable that Lebeau was the first to prepare the pure metal, which he did in 1894 by electrolyzing Na_2BeF_4 at a temperature below red heat, using a nickel crucible to contain

the electrolyte. This crucible also served as his cathode. The anode was graphite.

In 1915 H. Copaux took out French Patent No. 476475, which is based on fusing beryl with sodium fluosilicate. This process, sometimes with the addition of alkaline hydroxides or carbonates or of sodium fluoride, has since been followed by a number of inventors.

COMMERCIAL PROCESSES

In general, modern processes for beryllium production are based on bringing beryllium into solution as an alkaline fluoberyllate as initiated by Copaux, or as beryllium sulphate or chloride; usually, in the last named methods, dissolving the beryllium after a preliminary decomposition of the beryl by an alkaline hydroxide or carbonate or an alkaline earth oxide or carbonate. High-temperature chlorination has also been resorted to for the direct production of chloride, using chlorine, hydrochloric acid and carbon tetrachloride or various combinations of them.

The fluoride recovery processes take various forms, as the fusion with sodium fluosilicate as devised by Copaux spoken of above, or by attack by hydrofluoric acid at high temperatures, or silicon tetrafluoride at high temperatures, or in organic solvents; by treatment with ammonium fluoride both as a gas or in solution under pressure; by the use of acid sodium fluoride either under pressure or at high temperature; and, most recent of all, by the Kaweck process (U. S. Patent 2312297 of 1943) employing sodium-iron fluoride (iron cryolite).

All of these processes depend on the fact that the alkaline fluoberyllates are soluble in water, though beryllium fluoride is not.

As stated above, sulphate solutions are usually prepared after decomposition of the beryl with the alkaline or alkaline earth hydroxides or carbonates, though Sawyer (U. S. Patent 1823864) in 1931 claimed

the use of sulphuric acid on the beryl itself after heating to 1000°C. Jaeger and Wille in 1939 (U. S. Patent 2160547) claimed that beryl could be decomposed by treatment with sulphuric acid or acid sulphate if a small amount of fluoride was present but claimed also that only one tenth of the amount of the costly fluorine radical was necessary in this process as would be required for a complete decomposition of the beryl with fluorine.

One inventor rather dodges his responsibility by stating that he prepares a sulphate solution "in any well-known manner."

REDUCTION OF THE METAL

There is no outstanding method for the recovery of beryl metal any more than there is for the decomposition of the beryl. There are patents and processes covering the electrolysis of the beryllium fluoride or beryllium oxyfluoride ($\text{BeO} \cdot 5\text{BeF}_2$); for the electrolysis of beryllium fluoride in solution in molten calcium fluoride; and for the electrolysis of beryllium chloride in electrolytes in which the metallic base is more electropositive than the beryllium itself, such as sodium potassium, or lithium chloride. The electrolysis of beryllium iodide or beryllium chloride dissolved in anhydrous ammonia has also been patented by Booth, Torrey and Merlub-Sobel (U. S. Patent No. 1893221 of 1933).

The use of sodium or potassium to reduce beryllium compounds by experimenters working over 100 years ago has already been commented on. Magnesium has also been used either to reduce sodium fluoberyllate (Na_2BeF_4), NaBeF_3 or to reduce beryllium chloride.

Beryllium is like aluminum in that carbon reduction usually produces a carbide rather than metal. It also resembles aluminum in that the simultaneous reduction of beryllium and a base metal for the production of a master alloy can be performed by the use of carbon. Beryllium can also be produced in the same way that

magnesium can be produced, by thermal reduction with carbon; that is, by the volatilization of the reduced beryllium. Beryllium can also be reduced by carbon in the presence of hydrogen. Some experimenters have claimed that the hydrogen must be in the atomic form but the writer does not feel sure that this has been proved.

The extreme stability of beryl and the troubles encountered in decomposing it, as well as the difficulties met with in attempting to reduce any of the compounds of beryllium, due to the high electro position of beryllium in the scale of the elements, have already been commented on.

Other properties that make the metallurgy of this element a perplexing problem are: the metal has a high fusion point and a high vapor pressure at a temperature of not much above the fusion point; the pure metal is exceedingly light and has a tendency to float on slags and on fused electrolytes; the halides are all highly deliquescent and after they have absorbed water from the air, they cannot be reconverted to an anhydrous salt by simple heating, as all of the halides hydrolyze readily; when beryllium hydroxide is precipitated, it has a tendency to occlude and adsorb other salts and there is also a tendency to form basic and oxysalts. In short, beryllium deserves the characterization given it by Dr. C. B. Sawyer, of being "the world's No. 1 metallurgical headache."

PEROSA PROCESS

While it would be possible for anyone to construct his own flowsheet from the information that has already been given, it may be of interest to follow in detail the recovery of the metal by the Perosa process.

The beryl is heated and is then crushed and ground so that 100 per cent passes 100 mesh. It is then mixed with acid sodium fluoride in the proportion of four atoms of fluorine to one atom of beryllium, and this mixture is briquetted. The

beryllium is converted to sodium fluoberyllate, when the briquettes are sintered at from 650° to 800°C. The sintered briquettes are crushed and ground and leached with hot water. The filtered solution is then purified from iron, manganese and alumina by being made exactly neutral by the addition of sodium hydroxide, and a little potassium permanganate is added. The iron-manganese-alumina precipitate is filtered off and an excess of sodium hydroxide is added to the solution. Beryllium hydroxide is precipitated, filtered off, washed and dried. The drying temperature should not exceed the decomposition temperature of the hydroxide by more than a few degrees, for if it is dried at too high a temperature, its reactivity becomes less than if it is dried close to its

decomposition point. After drying, the material is ground in a paint mill with acid ammonium fluoride, which converts the hydroxide to ammonium-beryllium fluoride. The ammonium-beryllium fluoride is then briquetted and heated at a temperature sufficiently high to drive off the ammonium fluoride, leaving pure beryllium fluoride behind. This beryllium fluoride is then reduced with magnesium or a magnesium alloy in the presence of some of the metal of which it is desired to form a master alloy.

Because of the high cost of fluorine, no matter what the form in which it is obtained, the solution from the precipitation of the beryllium hydroxide must be treated to recover fluorine, as must also the slags from the final reduction.

Cadmium

By W. R. INGALLS,* MEMBER A.I.M.E.

METALLURGICAL literature has no record of any ore beneficiated for cadmium alone, and the cadmium of commerce is derived from zinc ore, with which cadmium is generally associated. Zinc ores free from cadmium—e.g., the ores of the Franklin and Stirling mines, New Jersey, and of Broken Hill in Rhodesia—are rare.

Blende concentrates of 50 to 60 per cent grade have contained (in production of important tonnage) as much as 1 per cent Cd, which is unusually high. The concentrates from the Tri-State district average from 0.3 to 0.4 per cent Cd, which is high. The concentrates from mines west of the Rocky Mountains seldom are higher than 0.2 per cent.

In the periodic system of the elements, cadmium is in the same group with zinc. Its properties and compounds are similar. Its metallurgy is also similar. Cadmium has a melting point of 320°C. and a boiling point of 778°C., while the melting point of zinc is 415°C. and the boiling point 905°C. These conditions, together with the lower reduction temperature of cadmium oxide, indicate means for separating cadmium from zinc.

Cadmium in spelter is viewed, if not as an impurity, at least as an alloying element that may be objectionable, its special effect being hardening. However, for some purposes, a little cadmium in spelter is desired, and 0.4 per cent may be permissible, even in spelter for rolling. Cadmium in

spelter for brassmaking is completely volatilized at the temperature of that process, and in bygone days an immense quantity of cadmium must have been lost in the fumes from these furnaces.

PYROMETALLURGY—EARLY

Cadmium compounds, sulphide and oxide, being more volatile than the corresponding compounds of zinc, loss of cadmium begins to occur from the first furnace operation. In normal roasting, even with Tri-State ore, this loss may not be very high. Raw ore, assaying 0.4 per cent Cd, may be expected to give a roasted product of the same assay, which would imply a cadmium loss of about 15 per cent. Roasted ore, assaying 0.4 per cent Cd when distilled at ordinary furnace temperature, yielded spelter containing about half of that in the ore charged.

The first draw of spelter under these conditions may assay 0.8 per cent Cd (accounting for 22 per cent of the cadmium recovery) and after the several draws of spelter have been equalized the cadmium content may average 0.35 per cent. If, therefore, 2000 lb. of blende averaging 0.35 to 0.4 per cent Cd is roasted and distilled, there may be obtained 1000 lb. of spelter, assaying 0.35 per cent Cd or 3.5 lb. content, which entering into Prime Western spelter will be sold at the spelter price.

It will be observed from the outline hereinbefore (summarizing conditions prior to the introduction of sintering) that the main loss of cadmium occurred in the distillation process and by failure to condense, which could be ameliorated by attaching a prolong to the condenser, thus collecting

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additional zinc dust, relatively rich in cadmium. This was the basis of cadmium metallurgy, especially practiced in Upper Silesia, prior to the introduction of the process of electrolytic zinc extraction. The primary zinc dust containing 5 or 6 per cent Cd, mixed with some charcoal, is distilled and redistilled until finally, by thus fractioning, a metal containing 99.5 per cent Cd is obtained. The low temperature of this distilling permits the use of cast-iron retorts and sheet-iron condensers, which are either lined with some refractory material or are whitewashed with lime inside, to prevent contamination by iron.

ELECTROMETALLURGY

With the introduction of the process of electrolytic zinc extraction in the U.S.A. and Canada in 1915-1916, that process became a large source of cadmium production, inasmuch as both cadmium and copper were bound to be leached along with zinc and necessarily had to be precipitated prior to zinc electrolysis. This purification is effected by adding zinc dust to the solution in such proportion as to throw down copper, which is filtered out and sent to copper smelting. Such a precipitate may assay 70 to 75 per cent Cu, 1 per cent Cd, and 3 per cent Zn (reflecting the excess of zinc necessarily used). To the filtrate, a large excess of zinc dust is then added, and the purified liquor is filtered off, leaving a zinc-cadmium sludge.

The zinc-cadmium sludge may be stockpiled in heaps, promoting oxidation and solubility in acid; or oxidation may be expedited otherwise—e.g., by spreading it on a platform and steaming it. Either way the cakes will probably have to be disintegrated, which may be accomplished by attrition in a pebble mill. There may have to be a precipitation of cobalt, requiring the use of some reagent—e.g., nitroso-beta-naphthol or potassium xanthate. However, the electrolysis of cadmium sulphate solution is not very sensitive

to impurities, and their removal by zinc-dust precipitation is generally adequate. It is impossible to wash all of the entrained zinc from the cadmium sludge, so zinc is a cumulative impurity in the electrolytic cycle. It is controlled by precipitation with milk of lime. It is only necessary to maintain the zinc in the electrolyte at a point where the excess of cadmium over zinc in the spent electrolyte is of the order of 10 to 15 grams per liter.

In the final stage of cadmium recovery, the sludge is dissolved in spent electrolyte and subjected to electrolysis, either with rotating cathodes or with stationary cathodes, which are of aluminum as in zinc electrolysis. Cadmium has a strong tendency to deposit as buds, sprouts, and trees. These are obviated by the use of rotating cathodes: or with stationary cathodes when cell temperature is maintained at 30° to 35°C. and with the addition of glue to the electrolyte. A deposition of 1 lb. of cadmium per 1.04 kw-hr. of direct current, compared with 1.5 kw-hr. for zinc, is realized. The plant factor, of course, is higher by virtue of the loss in changing from alternating current to direct current and the mechanical power that is required in plant operation.

In American practice stationary cathodes are generally used and with the same cell construction and operating conditions as for the electrolysis of zinc. With 3½-in. spacing between cathodes, the cell voltage is approximately 2.6 to 2.7 and the current density about 4 amp. per sq. ft., but in some practice as high as 10 amp. The cell feed may contain per liter 100 grams of cadmium, 80 of zinc and 70 to 80 H₂SO₄, and may be as high as 200 grams of cadmium and as low as 30 grams of zinc. Cathodes are stripped every 12 hr. in some practices; every 24 hr. in others. They are melted in a cast-iron pot, electrically heated to 400° to 450°C., under a thin layer of caustic soda to prevent oxidation, and the pot is well hooded to carry off oxide fume.

After the cadmium has been dissolved and is ready for electrolysis, the recovery as ingot is about 96 per cent. If the raw ore is roasted without special means for collection of dust and fume the over-all recovery may be 84 to 85 per cent. If the roasting furnaces are connected for sulphuric acid manufacture, with thorough provisions for collection of dust and fume, over-all recovery may be 90 to 95 per cent. Electrolytic cadmium is of 99.95 per cent in grade, or better.

HYDROMETALLURGY

In the use of roasted Tri-State ore for the manufacture of ordinary zinc lithopone, it is necessary to remove cadmium, just as it is for electrolysis. Such ore has been partially decadmiumized by a water leach, but that has not been a general practice, which is rather to take out the cadmium with an acid leach. From such a solution the cadmium is precipitated by addition of an excess of zinc dust, affording a zinc-cadmium sludge. As to purification, the requirements for a solution of zinc sulphate for lithopone are about as refined as for electrolysis. Digesting the sludge with sulphuric acid and obtaining a solution of CdSO_4 or $\text{CdSO}_4 + \text{ZnSO}_4$, the sulphides of those metals may be precipitated with a solution of barium sulphide to make cadmium lithopone; or a precipitate of cadmium sulphide may be thrown down from an acid solution by H_2S .

PYROMETALLURGY—RECENT

When the sintering process for desulphurizing and fritting zinc ores was introduced it was immediately noticed that the smoke issuing from the chimney dispersing the gases frequently showed the brown coloration of cadmium oxide, and concurrently that the cadmium content of the sintered ore was reduced or even eliminated all but entirely. It was observed, moreover, that following the introduction of roasters of the McDougall type, roasting flotation

concentrates with cyclones, improved dust-settling chambers, Cottrell precipitators, etc., as appendages, there was obtained dust and fume relatively rich in cadmium; e.g., as high as 4 per cent Cd and all of it water-soluble.

An experience with an ore containing 1.05 per cent cadmium, or 21 lb. per ton, following introduction of sintering, is illuminating. From a roaster of the McDougall type there was collected from 2000 lb. of raw ore 80 lb. of heavy dust assaying 4 per cent Cd. There was a further settlement of fume, but one pound of cadmium per ton of ore passed through the Glover towers and into the sulphuric acid. The calcines weighed 1700 lb. assaying 0.65 per cent Cd, and the sintered cake assayed 0.375 per cent Cd. The first draw of spelter weighed 204 lb. assaying 1.25 per cent Cd and the subsequent draws, aggregating 680 lb., assayed 0.08 per cent Cd. The cadmium accounting in terms of pounds per ton of raw ore was as follows:

In flue dust from roasters.....	3.2
In fume from roasters.....	5.8
In sulphuric acid.....	1.0
Loss in sintering.....	4.6
Content of first draw of spelter.....	2.6
Content of subsequent draws.....	0.5
Content of blue powder.....	0.5
Content of retort residue.....	0.2
Escape from condensers, by difference..	2.6
Total.....	21.0

It is clear that nearly all of the cadmium in this ore could be recovered by providing suitable means, especially for expelling all of the cadmium from the calcines (leaving none to go into the retorts) and collecting all of the dust and fume from both the roasters and the sinterers.

Such observations became the basis of the improved metallurgy among zinc distillers, who, in view of the increased demand for cadmium after 1935, aimed to recover the large cadmium content of Tri-State ore that previously had been wasted. In order to accomplish this the process of

sintering was adjusted so as to increase the elimination of cadmium, especially by preventing its condensation in the lower part of the bed on the pallets after it had been volatilized from the upper part, this being largely a matter of temperature control and technique. It was found also that by the addition of sodium chloride, anywhere from 0.5 per cent up to 2.5 per cent, the well-known chloridizing reaction could be realized, with nearly complete elimination of both cadmium and lead. Another expedient was moistening the ore with a solution of zinc chloride.

These proposals were founded on the idea of decadmiumizing and deleading zinc ore with the objective of producing high-grade spelter. At this time, about 1930 to 1933, cadmium was in poor demand. Later it became worth while for zinc smelters to save cadmium that previously they had been wasting. This involved, naturally, a reduction of the volume of the sintering gases by better sealing of the windbox and precipitation of their fume by means of Cottrells.

In works' practice the dust and fume from the roasters in oxidized form and the dust and fume from the sinterers, containing cadmium chloride, lead chloride and any of the excess of zinc chloride that has been volatilized, are mixed and digested

with sulphuric acid. Lead sulphate is filtered off. Cadmium may then be precipitated by the addition of zinc dust and the filtrate containing zinc sulphate and zinc chloride is returned to the sintering process, while the cadmium precipitate is refined by distilling, or otherwise.

By the New Jersey process of refining spelter by redistillation cadmium comes off in the form of cadmium-zinc metal, or a cadmium dust that is readily converted to metallic cadmium by any one of the several known methods. This was done prior to the war at Duisburg, Germany, by the Thede and New Jersey processes in combination.

In addition to the methods described hereinbefore, there is a good deal of cadmium produced by the silver-lead smelters, who in treating zinc ore obtain considerable quantities of cadmium in their flue dust. Treatment thereof for cadmium recovery has been sufficiently suggested without going into details.

Out of the production of metallic cadmium in the U.S.A. in 1941, aggregating 3220 tons, the electrolytic producers in Idaho and Montana afforded 970 tons. There is also a considerable production of cadmium obtained as direct chemical compounds, especially cadmium sulphide, for which there is use as a pigment, either as such alone or in cadmium lithopone.

Modern Plants for Reduction of Quicksilver

By GORDON I. GOULD,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1944)

THE treatment of quicksilver ores to extract the metal, for centuries one of the fundamentally simpler metallurgical operations, has undergone few if any material changes during the past few decades other than improvement and change of type of equipment used. Of almost universal application and as the seldom deviated from process, the roasting method is still considered superior to chemical metallurgy. Likewise, roasting of the crude ore without previous beneficiation continues to be standard practice, although some successful operations have employed concentration prior to roasting.

The roasting process has been carried out in a variety of equipment, devised for different tonnage capacities, to treat "special" ores, and to satisfy an inventive notion of the particular builder, but during the past 25 years there has been one outstanding change in roasting equipment.

This change, though neither originating in nor confined to the United States, has probably been developed and applied to a far greater extent in this country than in any other mercury-producing country of the world. The change from manually or gravity operated furnaces, mostly huge brickwork affairs justified largely by simplicity, lack of power and mechanical requirements, and occasionally by excellent metallurgical results, to mechanical furnaces, began actively during World War I under the stress of requirements for in-

creased production, a shortage of labor, and other factors to be brought out later.

During the twenties the change to mechanical furnaces became nearly complete at American mines with the development of several types, the rotary furnace predominating. During the thirties, and the period of low prices in the early part of this period, few changes were made other than mechanical improvements and an almost complete acceptance of two types: the rotary furnace and the hearth or Wedge furnace. These two types have been developed to a high degree of metallurgical efficiency, have proved to be mechanically simple and have far greater flexibility and lower operating costs than pre-World War I furnaces. Of the two types the rotary is the more popular, about 30 rotaries having been in operation in the United States in 1943 as compared with about six hearth-type furnaces.

The units of smaller capacity for roasting mercury ores have almost without exception been indirectly fired, such distinction being commonly accepted as the difference between retorts and furnaces, which are fired directly. The difference between indirect and direct firing obviously permits of quite different conditions surrounding the ore being roasted in relation to the chemical reaction to take place. In the indirect-fired unit the ore is contained within the body of the retort in a stagnant if not completely oxygen-impoverished atmosphere. In the direct-fired furnace the ore is in contact with the gases of combustion, which may easily (if not too easily) be supplied with an excess of

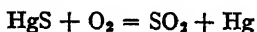
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* H. W. Gould & Co., San Francisco, California.

oxygen, providing for excellent oxidizing conditions.

Inasmuch as cinnabar, the most important ore mineral of mercury, and meta-cinnabar, found separately or together with cinnabar in many deposits, are both sulphides of mercury (HgS), it is obvious that somewhat different reactions will take place in the retort and in the furnace. In the retort the cinnabar must be heated to approximately 1075°F. , its sublimation temperature, at which heat mercuric sulphide vapor will leave the charge. Unless recrystallization of the mercuric sulphide is to occur at the lower temperatures existent in the condenser pipes, something must be made available to combine with the sulphur released and free the mercury. For this lime or scrap iron is often used, although in practice frequently nothing is added to the ore but dependence is placed on either a natural or forced ventilation of the retort to provide sufficient oxygen to combine with the sulphur. When the amount of oxygen so supplied is insufficient, the very walls of the retort are attacked and gradually reduced to such an extent that they fail.

In modern furnace operation the gases of combustion and as much excess air as is desirable is brought in direct contact with the ore being roasted. Under these conditions and because the vapor pressure of mercuric sulphide permits the release of mercury at relatively low temperatures (450° to 500°F.) oxidation of the sulphur takes place. This permits operation at temperatures below those required for retorting, but in practice furnace temperatures usually run to a maximum of 1250° to 1600°F. , in order to speed the dissociation, make a more complete extraction, and increase capacity of the furnace. Because of the presence of adequate oxygen, fluxes are not used and the chemical reaction that takes place may be represented as:



It is apparent that, chemically, it is only necessary that sufficient oxygen be supplied to oxidize all of the sulphur in the ore (exclusive of that required by the fuel or for the oxidation of other constituents of the ore), but excess quantities are always carried in order to ensure complete oxidation.

A feature of the modern mechanical furnace as contrasted with the older brickwork units is that in all of them positive means are employed to agitate the ore, bringing it repeatedly in contact with the air stream, and thereby reduce the excess quantities required. In the older furnaces of the Cermak-Spirek, Scott, Knox-Osborne, Bustamente, or other types, the ore was for greater periods of time stagnant, out of contact with the air, or a channeling of air through the charge left certain portions impoverished of oxygen. Such a condition often resulted in incomplete dissociation of all of the cinnabar or caused the formation in the condenser chambers of oxygen-deficient mercury-sulphur compounds.

Assuming proper operation, the necessity for such an occurrence is largely avoided in the rotary furnace by the cascading of the ore as it travels down the kiln during rotation. The ore is continually rolled over and brought to the surface of the bed; escaping vapors are permitted to leave the particles and, at the same time, air is permitted to contact new surfaces of the particles. A somewhat different type of action, with the same result, is effected by the raking action of the rabble arms of the hearth-type furnace as the ore is raked first to the outside of the hearth then back to the center on the next hearth below.

In practice, it is obvious that it would be neither desirable nor most efficient to expose the ore to only the theoretical amount of oxygen required for oxidation of the sulphur contained in the cinnabar: (1) because of the mixed sizes of ore fed

to various furnaces, complete contact of all cinnabar with air cannot be obtained economically within the contact period; (2) dissociation can be obtained more quickly with excess quantities of oxygen; (3) because the "sweeping" effect of a larger than required volume of air permits of greater capacity; (4) because of the requirement for fuel combustion and for oxidizing other constituents of the ore such as sulphur contained in other forms, or antimony, arsenic, etc.; and (5), probably most important, because of the varying nature of the feed, accurate control of the theoretical amount of air required would be a near impossibility, so that an excess is a safety factor.

The modern mechanical furnace, therefore, applies the same principle in adding excess air as was used in the older furnaces, but through better contact is able to reduce such excess and thereby increase capacity, reducing fuel consumption and permitting equal or improved recovery.

In construction both the rotary type and the hearth type of furnace lend themselves to a variety of sizes, designed to handle varying tonnages and to suit special conditions. Although furnace sizes normally are rated at tonnage capacities, the weight of the ore, size of feed, moisture content and other volatile content are factors that influence the capacity. These factors, however, frequently affect other units beyond the furnace to a far greater extent than they do the furnace proper.

ROTARY FURNACES

One manufacturer of rotary furnaces for reduction of quicksilver ore* lists the following standard sizes and capacities:

DIAMETER, IN.	LENGTH, FT.	TONS PER 24 HR.
21	18	8-12
24	24	12-25
36	40	25-40
36	48	40-60
48	64	60-100
60	84	100-150

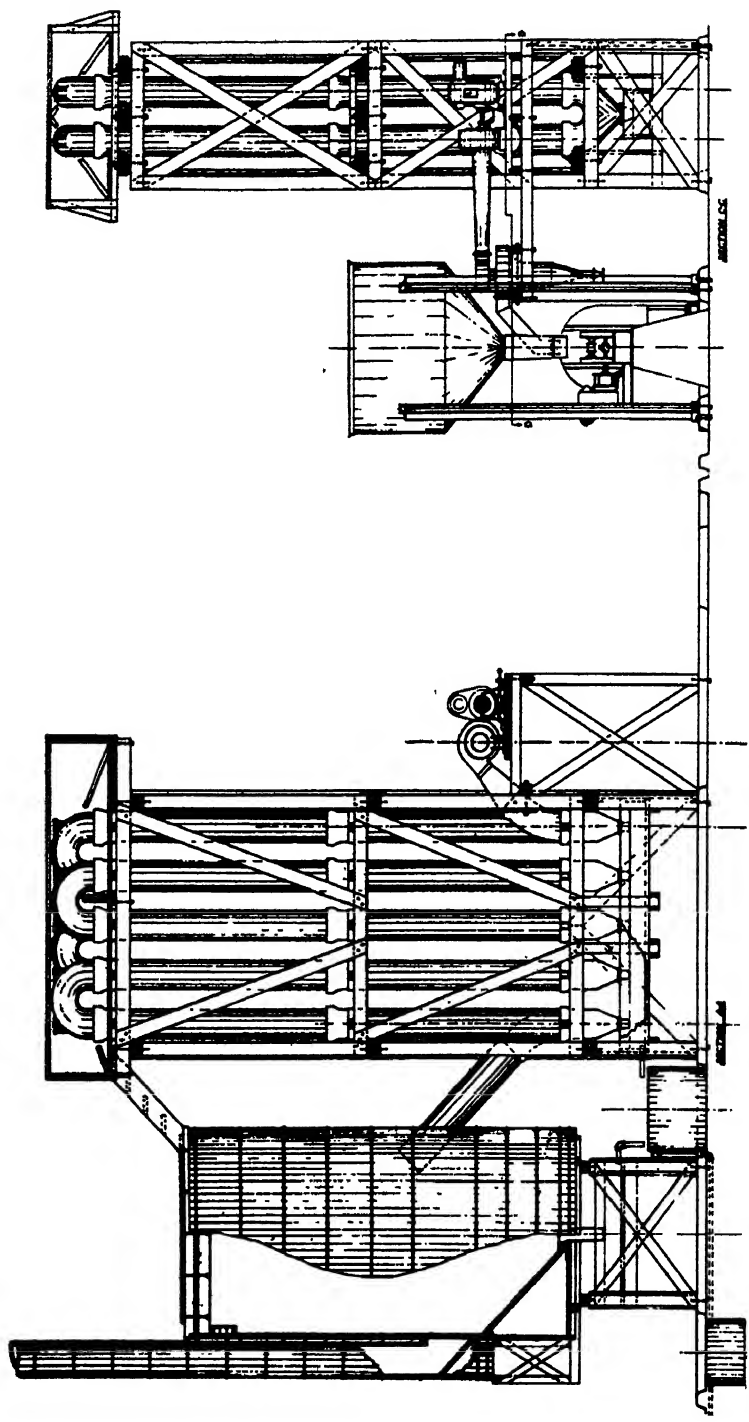
* H. W. Gould & Co.

Fig. 1 illustrates a 12-to-25-ton kiln with dust-collecting equipment, exhaust fan, condensing system, settling tank and stack.

The diameter of the furnaces listed above is the diameter of the shell; a 4½-in. firebrick lining is used in all furnaces except the 60-in. size, which uses a 6-in. lining. Furnaces vary in inclination from ⅝ in. per foot on the largest size to 1¼ in. per foot on the smallest size. Furnace speed of rotation varies from about 32 sec. per revolution to 75 sec. per revolution; the larger furnaces usually, but not always, revolving more slowly. Power requirements vary from ¾ to 7½ hp., the power being transmitted through V-belt drive and a worm-gear speed reducer to a pinion gear and the ring gear on the furnace. Notable improvements in furnace fabrication have been the employment of antifriction type bearings throughout, improved seal rings or expansion joints, and the use of alloy steels and special irons for ride and drive mechanism.

Although both parallel-flow and counter-flow furnaces are used in quicksilver metallurgy, the latter is the more common. In this type the ore is fed into the upper end of the furnace, travels downward, and is discharged at the lower end. The heat is applied at the lower end of the furnaces and the gases of combustion and volatile products are drawn off through the upper end of the furnace. In this type of operation the ore is gradually brought up to a maximum temperature before discharge and the excess heat in traveling up the furnace is used to dry and preheat the ore, thereby lowering gas-discharge temperatures. A short distance at the extreme low end of the furnace is beyond the maximum temperature zone and suffices for the sometimes required soaking zone. The length of this zone may be regulated by the flame length.

In the parallel-flow type of operation, used at the Sulphur Bank and Reed mines in California, the ore is both fed and fired



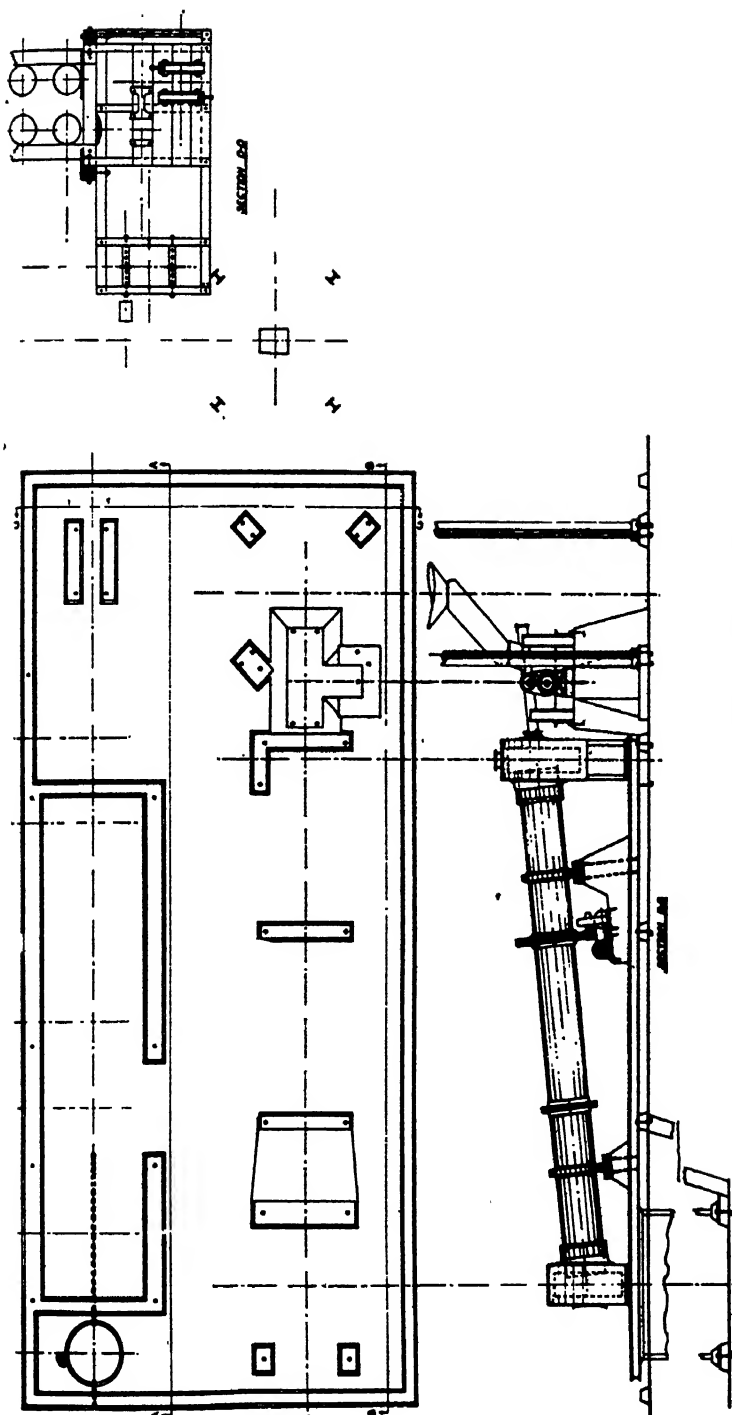


FIG. 1.—GOULD ROTARY FURNACE AND CONDENSER SYSTEM.

at the upper end of the furnace and calcine and gases are discharged at the lower end. Although this system increases fuel consumption and gas-outlet temperature, it seems desirable at the Sulphur Bank mine because of the high content of free sulphur in the ore and at the Reed mine because of high sulphur and a large amount of petroleum in the ore. Following the more customary method of firing, a large amount of the sulphur and petroleum "smoked" over into the condensing system, thereby presenting a difficult problem in quicksilver cleanup.

Various types of seals or expansion joints have been used for making a relatively airtight seal where the rotary furnace enters the hood at either end. This is desirable principally to prevent the admission of uncontrolled excess air.

FEEDING ROTARY FURNACES

Ore feeders have probably varied more than any other single unit of the rotary kiln plant, and have included screw, pan conveyor, chain conveyor, vibrating, shaking and straight chute types, each with its own variations. The principal reason for this lies in the fact that unsized material, sometimes up to 3 in., varying in character from sandy and dry to wet mud, may be the material to be handled.

The most popular type is the shaking feeder consisting of a tube ranging from 5 to 10 in. in diameter, which extends through the upper hood and into the furnace. This pipe is supported on rolls or slides, outside the hood, and is set at an inclination of approximately $1\frac{1}{2}$ in. per foot. A hopper at the upper end of the pipe receives the ore, usually by gravity, from a chute and fine-ore bin built directly over the feeder. A cam draws the pipe back and springs pull it forward against a bumper block, the sudden jar throwing the ore forward and into the furnace. A seal where the feeder pipe enters the hood prevents leakage of gases at this point,

and with the pipe kept full of ore it is possible to maintain a gastight seal throughout. Power required ranges from $\frac{3}{4}$ to $7\frac{1}{2}$ hp. and all modern installations are equipped with variable-speed drives to permit regulation of feed.

In the parallel-flow furnaces such as are used at the Sulphur Bank and Reed mines, the same type of feeder using only one half the pipe section, and not requiring any seal where the feeder enters the hood, has been used successfully. At the Mt. Diablo mine, California, an inclined pipe chute fed by a conveyor discharges the feed onto the upper end of the furnace, the pile thus created being carried away by the rotation of the furnace. With proper draft control no leakage of gases occurs and its use here has been successfully demonstrated.

FIRING ROTARY FURNACES

There is probably nearly as much diversity in the firing as in the feeding of quicksilver-reduction plants. Fuels have included wood, petroleum fuels (from 12° to 27° Bé gravity), coal, and natural gas, but wood and oil of 16° to 24° Bé gravity have predominated. It was not until World War I that oil began to replace wood in the brickwork furnaces. Since that time it has become the almost universal fuel except in isolated instances where others of those mentioned have been cheaper.

In the firing of rotary furnaces, the two principal opinions on oil firing support either high-pressure or low-pressure burners. Although the former is more generally used, an increasing interest is being shown in the newer improved burners of the so-called low-pressure type. This may be due in part to the aggressiveness of manufacturers of low-pressure burners who are attempting to make more scientific application of their equipment, a point that users of high-pressure burners have recognized and applied to their own equipment. It is not within the scope of this paper to

attempt to answer this question, but it is interesting to note that, exclusive of burner type and character of ore, oil consumption varies from approximately $4\frac{1}{2}$ gal. per ton of ore burned at the New Idria mine, California, to 20 gal. per ton in furnaces of the parallel-flow type. It is probably safe to say that average oil consumption will run between 6 and 7 gal. per ton.

Normally the smaller furnace will consume up to 10 per cent more fuel per ton than the larger sizes treating the same material, and it has been found that furnaces of 24-in. diameter or smaller operate with more flexibility and uniformity when using fuel of 24° Bé gravity. The larger furnaces operate smoothly and cleanly on fuels of 16° to 18° Bé gravity.

In the average oil-fired rotary, the burner (either high-pressure or low-pressure) is mounted in the hood to extend toward or even into the furnace. Various types of burner tips regulate the flame length and the burners are nearly always adjustable as to vertical or horizontal angle to obtain the maximum heat on the ore. High-pressure burner equipment usually utilizes compressed air for atomization with various methods used for controlling, heating, and admitting secondary air. In many operations the air is preheated by ducts through or around the burnt-ore bin, directly under the hood at the discharge end of the furnace. In the low-pressure burner installations, atomization is accomplished by air from low-pressure blowers, which admits regulated primary air and oil through the nozzle. Secondary air is supplied in much the same manner as to high-pressure burner installations.

In either type of installation, oil may or may not be supplied under pressure. Power required for compressors for high-pressure burners ranges from 3 to 30 hp. through the sizes of furnaces mentioned, and approximately the same power is required to drive the blowers for the low-pressure burner equipment.

Next in importance in new installations are the wood-fired rotaries. First was the installation at the Pinchi Lake mine, British Columbia, where two 4 by 60-ft. furnaces were installed. It is reported that the grate area is approximately 40 sq. ft. in a box something over 7 ft. high. A 24-in. square opening 3 ft. above the grates admits the fire, through an 18-in. wall, to the furnace, after it passes over an ore-discharge chamber about $3\frac{1}{2}$ ft. wide. It is reported that satisfactory roasting was accomplished with this firebox, with a wood consumption of one cord per 11 to 13 tons of ore burned. An undesirable wood-tar residue, however, formed in the condensing system, due to incomplete combustion, and this caused so much trouble that the rotaries eventually shut down and converted to low-pressure oil firing.

A 3 by 48-ft. rotary furnace was installed at the Takla mine, British Columbia, and equipped for wood firing with 24 sq. ft. of grate area in a box 6 ft. high. A 6-in. round hole 4 ft. 6 in. above the grate admits the fire to the furnace through a 9-in. wall, and across a 16-in. ore-discharge chamber at an elevation 6 in. below the furnace center line. Although no details are available, it is reported that this furnace functions very satisfactorily at 60 tons daily capacity.

A 3 by 40-ft. rotary furnace installed at the Red Devil mine, Alaska, operated very satisfactorily at a wood consumption of one cord per 12 tons, burning all the wood tars and admitting clean, hot air to the furnace, using a somewhat differently designed firebox. A long fire and combustion box 3 ft. wide by 18 ft. 9 in. long, inside measurements, was built at the end of and parallel to the furnace. The lower 6 ft. of this box provided 18 sq. ft. of grate area. This box was 3 ft. 6 in. high. A baffle wall 9 in. thick and 2 ft. high divided this compartment from the combustion chamber, which was 6 ft. long and 2 ft. 9 in. high,

its floor being 9 in. above the grate level. A 5 by 9-in. hole $2\frac{1}{2}$ in. above the floor of the combustion chamber permitted the fire, after burning on the grate and passing over the baffle, and traveling along the length of the combustion chamber, to pass through a $4\frac{1}{2}$ -in. wall, across a 9-in. wide ore-discharge chamber and into the furnace just above the elevation of the brick lining in the furnace.

It should be pointed out that the wood-fired furnace, though not popular where oil is easily available, may have a place in new discoveries possibly to be made in remote areas away from transportation. Those mentioned have not been able to obtain sufficient oil during wartime conditions and may later be converted. Likewise, because the burning of wood forms nearly twice the volume of gases of combustion, wood-fired plants treat only about one half the tonnage of similar plants that are oil-fired.

The coal-fired plant was 2 by 24 ft., installed at the Chonta mine, Peru, where local coal was used because of the excessive cost of transportation. The natural-gas-fired plant was 4 by 64 ft. and was installed at the Valley View mine, California. This provided an enviable, cheap, clean fuel not requiring auxiliary equipment, and of the simplest type to provide with automatic control.

MULTIPLE-HEARTH FURNACES

A manufacturer of hearth-type furnaces for the treatment of quicksilver ores* reports the following sizes as standard equipment:

TONS PER DAY	SIZE	NUMBER OF HEARTHS
2	36" i.d.	8
20	10' 0" o.d.	4
30	10' 0" o.d.	6
50	13' 6" o.d.	6
75-100	16' 0" o.d.	6

The hearth-type furnaces consist of a cylindrical metal shell, which supports

conical or spherical arches of firebrick decked one above the other. A vertical central shaft, running through the center of the shell and brick arches, carries rabble arms on the various decks, which rake the ore across the decks. The feed is at the top, either at the center or on the periphery of the shell, and the ore is raked first inwardly then outwardly as it drops to the deck below. (The raking action might be reversed, depending upon whether the feed started at the center or on the periphery.)

The hollow central shaft is carried on heavy bearings and is rotated by a bevel gear drive at the bottom, further reduction being obtained by a gear-reduction unit. The speed of rotation of this shaft normally ranges between 45 and 60 sec. per revolution and power required is 2 to 3 hp. in the various sizes. This shaft is hollow, in order that cooling air may be blown through an inner pipe, out through the rabble arms and back into the central column outside the inside pipe, and thence to waste or for use as preheated air in the hearth areas. The power required to supply this cooling air is 3 hp. Notable improvement in the furnace construction in modern installations includes the use of heat-resisting metals for the construction of the rabble arms and raking teeth to give them greater life. With adequate air cooling and design to permit of simple changing, these items may be changed during operation with very little lost time.

The ore is fed at the top of all furnaces of this type, so that the ore must be elevated. In the Herreshoff furnace, which is the most popular hearth type, the ore is fed into a hopper, which drops it onto a shelf from which it is "wiped" off by a feed knife attached to the top rabble arm.

Ore feed to furnaces of this type is usually more closely sized than that necessary for rotary furnaces. No operations are known to the writer where feed size exceeds $1\frac{1}{4}$ in. At the Bonanza mine, Oregon, where a hearth furnace was first installed,

* Pacific Foundry Co., Ltd., San Francisco.

and subsequently two rotary furnaces, the ore was screened, all minus $\frac{3}{4}$ -in. going to the hearth furnace and the plus $\frac{3}{4}$ -in. to the rotaries. At the Pinchi Lake mine, the feed to the two rotaries was minus 2-in. plus 1-in. and that to the three Wedge furnaces was minus 1-in. The speed of rotation of the central shaft is seldom changed, but the rate of feed at the feed point and the depth of bed on the different hearths can be changed by changing or varying the pitch of the rakes on the rabble arms.

Firing, with one known exception, of hearth furnaces used in reduction of quick-silver ore has been with oil fuel. This one exception, at the Pinchi Lake mine, used wood and/or oil.

In the multiple-hearth furnace it is common practice to use one or more of the top hearths for drying or preheating the ore, the next one or more hearths for the roasting of the ore and one or more hearths for soaking or cooling before it is finally discharged. In this practice it is common to fire through ports in the shell on one or more hearths in the roasting zone only. Low-pressure oil burners are commonly used.

It is reported that at the Pinchi Lake operation the initial installation included fireboxes for wood on either side of the Wedge furnaces with ducts to the ports on the various hearths. Because of the difficulties encountered with wood tar in the condensing system, previously mentioned, it is reported that a final installation made possible firing with one half wood and one half oil fuel.

At the Cordero mine, a new 13-hearth Herreshoff three-zone furnace, 14 ft. 3 in. in diameter (Fig. 2), is of interest in that an attempt has been made to utilize, to as great an extent as possible, waste heat in air used to cool the central shaft and rabble arms and waste heat from the roasted ore.¹ The three zones refer to a drying zone

consisting of the top three hearths, a central heating zone consisting of eight hearths (the top two for preheating, the next four for roasting, and the bottom two for soaking), and finally two cooling hearths at the bottom of the furnace.

Cooling air is forced up the central column and some is forced out through the rabble arms on the cooling hearths. This part, together with air admitted through a port in the shell, is drawn off these two hearths through four ducts running to the bottom of the drying zone where it is passed over the wet ore.

Another portion of the central-column cooling air is forced through the rabble arms of the two soaking hearths, to combine with additional air admitted through a port in the shell to provide secondary air for the central heating zone. This air, together with the gases of combustion and volatile products, is drawn off the top of the central heating zone and sent through dust-collector and condensing system.

Finally, the remainder of the central-column air is forced through the rabble arms of the burner and preheat hearths without escaping to the atmosphere of the central heating zone, and thence through the holes in the rabble arms of the top drying zone directly on the ore. In this zone it combines with air preheated in the cooling zone and is drawn from the top of the furnace by a separate exhaust fan and sent to waste.

It is reported that fuel savings up to 40 per cent over the conventional single-zone installation can be obtained by this system and a capacity of 125 tons or more obtained.

Beyond the furnaces, similar practice, with variations, is followed in nearly all plants. The ore has been roasted and discharged and the mercury-rich gases leave the furnace containing ore dust, water vapor, mercury vapor, and other volatile products of the roasting operation. This calls for a dust-collecting unit, exhaust fan,

¹ References are at the end of the paper.

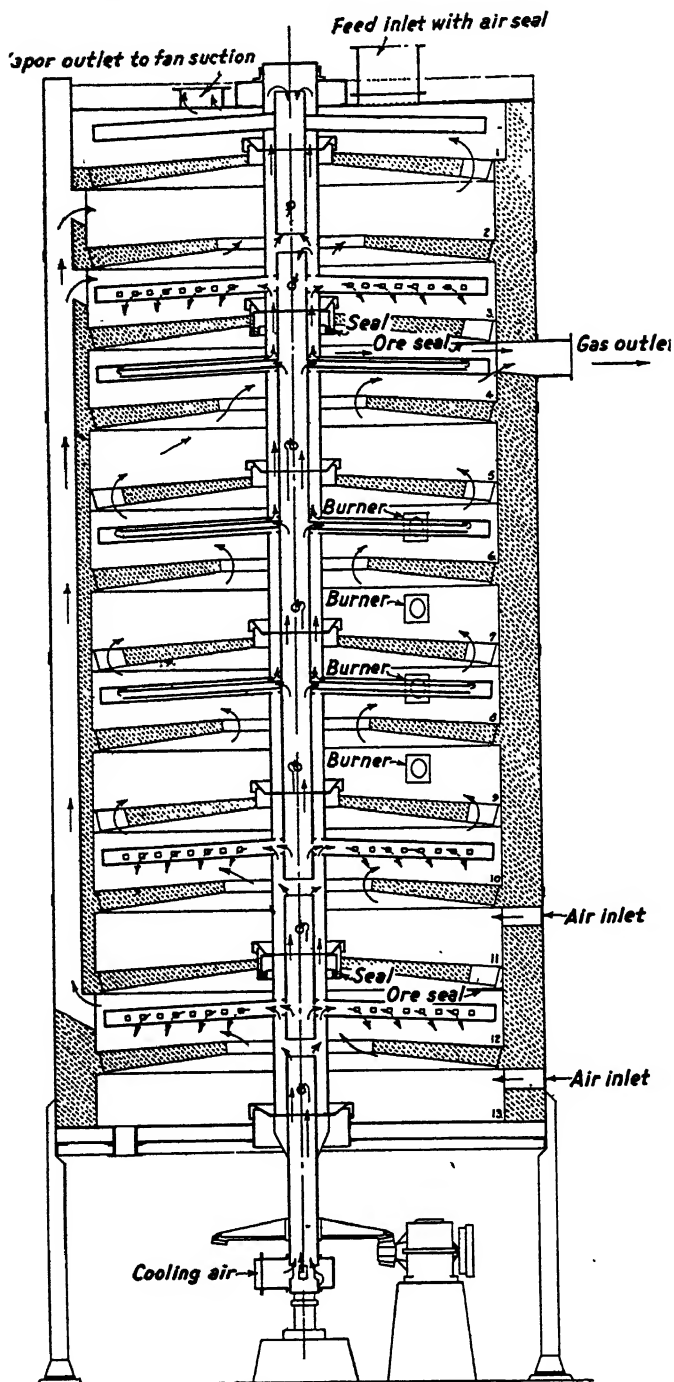


FIG. 2.—NICHOLS-HERRESHOFF FURNACE. ARROWS INDICATE DIRECTION OF AIR AND FUMES.

condenser, final settling chambers, and stack.

DUST-COLLECTING EQUIPMENT

In the middle twenties the cyclone type of collector was first applied to the collection of dust from quicksilver-reduction plants, and it has gained almost unanimous American approval. The low first cost and satisfactory performance of these collectors have given them first call over other types. Two Cottrell electrostatic precipitation collectors were installed, one on a hearth furnace and one on a rotary furnace, but it is not believed that the results were commensurate with the first cost and maintenance. Whatever type of collector is used, it must be sized with a full cognizance of the gas volume to be handled and the temperature of operation. Normal operating temperatures with the cyclone collector following the furnace vary from 400° to 700°F.

EXHAUST FANS

Exhaust fans, for drawing the gases through the furnace, are in most instances placed after the dust collectors, to draw the gases through them and force the gases through the condensers, settling tanks and stack. Some operators, however, prefer to place the exhaust fans between the condensers and settling tanks or stack. The operation of the condensing system under a positive or negative pressure, in either case very low, seems to be a matter of personal preference rather than one of great importance.

CONDENSING SYSTEMS

Common American condensing practice for the old brickwork furnaces utilized large brick chambers, in which the quicksilver condensed and settled out, always together with large volumes of mud (from the ore dust) and not infrequently with soot from the fuel (and sometimes sublimed sulphur).

Fundamentally, the brick or masonry chamber with walls approximating a foot in thickness (of good insulating quality) was not the most efficient type of condenser.

The first important change substituted a series of vitrified-tile sewer pipe, set on a 45° angle, so that the gases would be cooled during their travel up and down their length, and cause the mercury therein condensed to run by gravity to a junction box, for simplified cleanup. This system improved the thermal efficiency of condensing systems materially and simplified cleanup to a very large extent.

With the application of dust collectors for removal of ore dust from the gas stream, the next step was the change to metal pipes, set vertically, and arranged with simple water seals at the lower end for easy cleanup, and with hand holes at the top for simple washdowns. The corrosive qualities of the gases were early recognized and accepted as a matter of course, and in recent years a definite attempt is being made to understand in advance the extent to which ores of any particular type may make a corrosive gas. This is largely predetermined on the basis of experience, ore analysis, moisture content, and other factors.

Materials used in vertical pipe condensers include vitrified-tile sewer pipe, sheet steel, Monel metal, cast iron, and stainless steel. Of these, the cast iron is the most popular, largely because of its low cost for the life it affords. One manufacturer, who used only 16-in. diameter pipe, used a centrifugally cast iron, on which there ranges a life of from a minimum of two years to a maximum of about six years. In modern installations, the vitrified pipe is usually used with other materials, inasmuch as it does not have as high a rate of heat transfer as the metals, does not have the ability to withstand thermal shock, but does have a high resistance to corrosive attack. Sheet-steel systems have proved their economic worth in applica-

tions where sulphur content of the ore is very low or where a short life is justified. They are used also in combination with other materials. At least two Monel-metal systems have been installed but have showed no principal advantage over sheet metal (cost vs. life). Stainless steel has been used, together with black iron and cast iron, in a modern installation at the Cordero mine, with very good results.¹

Although most condensers use a 16-in. diameter pipe, sizes range down to 8-in. diameter, regardless of the material used. The length or the area of the system varies in accordance with the size of pipe used, tonnage being treated, and heat transfer required, and there seems to be no general rule as to the area required.

Two important factors in this determination are the baffling effect created by the sudden reversal of direction of the gases passing through the system and the amount of buildup of soot or mud on the condenser walls. The benefit of baffles in a condenser where it is possible to knock down precipitated (or condensed) product is recognized. Despite theoretical condenser area required, this point may be one of major importance. Likewise, if a condenser tube of too small a diameter is used, building up of soot occurs on the walls of the tubes, and not only is thermal efficiency impaired but the back pressure of the system is built up to a point where tonnage capacity and metallurgical efficiency are reduced.

A typical condenser system on a plant rated at 40 to 60 tons daily capacity consists of thirty-two cast-iron pipes, 16 in. in diameter by 12 ft. long, set two pipes high in sixteen stands. These are connected at the bottom by nine cast-iron hoppers and at the top by eight cast-iron return els. The length of this system is approximately 452 ft. and the area roughly 2011 sq. ft., or 7.53 ft. of length per ton of maximum capacity, or 33.5 sq. ft. per ton of maximum capacity.

During normal operation a certain amount of soot (the general term used to describe the condenser product ranging from 20 to 85 per cent Hg, containing free mercury, ore dust, fuel residues, or other volatile products such as sublimed sulphur and oxides of arsenic, antimony, etc.) is collected, through a water seal at the bottom of the vertical pipes, in buckets or an open launder and goes to further cleaning, and some of it hangs up on the walls of the condenser pipes. This "hangup" is periodically washed down for collection and further cleaning, and to clean the walls of the condensers and restore maximum condenser efficiency.

Most often the soot is collected in buckets at the bottom of each stand or row of pipes but at the Mina mercury mine, Nevada, and the Pinchi Lake mine, screw conveyors have been installed to transfer and dewater the soot for further cleaning. (The further cleaning consists of mixing the soot with quicklime and hoeing, either manually or by mechanical means, until the bulk of the free mercury is released and ready for flasking. The hoed soot usually is returned to the furnace but in some operations it is retorted for final recovery of all quicksilver.)

SETTLING TANKS AND STACK

General practice favors the installation of one or more settling tanks following the condensing system. These usually are wooden tanks varying in size from 5 ft. in diameter by 12 ft. high to 14 by 20 ft. In these, the gases are expanded, with reduction in velocity, thus permitting the settling out of finely divided quicksilver carried in suspension on particles of dust or water vapor, and acting as a safety factor for faulty operation involving excessive temperatures or draft through the system. Although the tanks usually are simple settling areas, they are sometimes equipped with water sprays, grids, baffles

or other devices for ensuring maximum collection.

From the settling tanks, which occasionally are omitted entirely from the flowsheet, gases are always eliminated to waste through a stack, usually of wooden construction, to avoid corrosive action. Final stack temperature is variable and depends on the size of the condensing system, water vapor, atmospheric temperature, etc. Although it may range from 45° to 160°F., it is probably safe to say that the average plant will run a stack temperature of from 100° to 140°F. For good operation with low stack loss, 140°F. should not be exceeded.

CONTROL

In the modern quicksilver plant, indicating or recording instruments usually measure temperature and draft conditions at one or more strategic locations in the flowsheet. This simple control, necessitated by the nonuniformity of ore feed characteristic of average quicksilver ore, usually suffices, when augmented by experienced operation, to provide for safe and satisfactory metallurgical efficiency. It may safely be stated that either the rotary or hearth type of furnace, with properly designed condensing system and auxiliary equipment, and when properly and conscientiously operated, will recover in excess of 95 per cent of the value of the ore feed with regularity.

Labor and fuel are the principal cost items. Average fuel consumption has already been given. Labor required in a modern plant has been reduced to a minimum. Usually one furnace operator per furnace per shift, plus one to two additional men for crushing, cleanup, or general labor on the day shift, are sufficient. Under present conditions of high labor costs, with certain wide variations, it is difficult to give average figures; however, they may be said to range from \$1.00 to \$3.50 per ton. Probably the average cost

per ton of ore treated is between \$1.50 and \$2.00, exclusive of plant amortization.

In point of initial cost, the same variation due to wartime conditions exists. The cost per ton of daily capacity probably will range between \$500 and \$1000 for rotary-kiln installations and slightly higher for hearth-type kiln installations. Transportation, availability of power, labor, and building supplies might cause appreciable deviation from these figures.

RETORTS

The retort production of quicksilver is confined usually to operations in which only a small quantity of high-grade ore or concentrates is obtainable, for the purpose of cleaning up soot from furnacing operations, or for reclamation of secondary mercury in the scrap or chemical field.

Although there are several types of retorts, the most popular (and most efficient) is the cast-iron pipe made in a \square section, 12 in. high by 20 in. wide by 108 in. long. This type is the only one used in all three of the operations mentioned above and probably is the most satisfactory for each. Mounted in a brickwork with heating flues under and over the pipe for oil, gas, wood or coal firing, it is charged with from 250 to 750 lb. of material per charge, each charge being confined in the retort 8 to 18 hr. The volatile mercury, by natural or forced draft, is carried out of the retort into a downwardly inclined condenser pipe, often water-cooled, 4 in. by 8 ft., in which the quicksilver condenses. These units are set up singly or in pairs and normally consume approximately 20 to 25 gal. for a single pipe and 35 to 40 gal. for a double pipe, per day, of fuel oil or corresponding equivalent in other fuels.

Round pipe retorts, mounted similarly except for feeding at one end and discharge of vapors at the other end, are sometimes set up with as many as 12 pipes. This type, generally known as the Johnson-

McKay type, is widely used because of its simplicity.

The Rossi retort, and similar types, consist of inclined round pipes into which the ore is fed at the upper end and discharged periodically at the lower end by gravity. They have won considerable favor, though diversity of design has detracted from their average efficiency.

CONCENTRATION BEFORE ROASTING

Various concentration plants have been built to make a concentrate for either retorting or furnacing. Although many of these have met with varying degrees of success, three typical types of installations will be mentioned.

One of the simpler types, designed for rough concentration at low cost, was used at the New Idria mine. It consisted of feeding $1\frac{1}{2}$ to 3 lb. Hg per ton ore (mostly old mine dumps) over a grizzly and on to a shaking screen. All oversize from the grizzly, set at 2 in., and from the screen, set at $\frac{5}{8}$ -in., was sent to a waste conveyor belt where coarse high-grade was hand-sorted off the belt. The fines from the screen were passed over a 36-in. Bendelari jig, making a high-grade hutch product and low-grade bed product, the average of which ran between 6 and 10 lb. per ton. This material was then combined with mine ore to augment the furnace feed. The large quantity of material handled at low cost, despite relatively low metallurgical recovery, proved economically successful on an otherwise uneconomic material.

A more conventional milling operation at the Sain Alto mine, Zacatecas, Mexico, was the Denver Equipment Company's installation² of a successful flotation plant for the recovery of high-grade concentrates, which subsequently were retorted for final recovery of quicksilver. This operation consisted of flotation after closed-circuit grinding to minus 65-mesh and 3-min. conditioning, with a final cleaner cell before the filter. The depression of carbonaceous

material and arsenical minerals was a special problem with this ore. On a measured period, ore averaging 0.67 per cent made a concentrate of 46.21 per cent with a recovery of 95.4 per cent.

A third and somewhat different problem was that of the Huitzuco mine, Guerrero, Mexico, wherein the quicksilver occurred in the mineral Livingstonite, a double sulphide of antimony and quicksilver. This plant used flotation to recover a Livingstonite concentrate, which subsequently was treated for the recovery of both antimony and quicksilver.

Numerous small operations utilizing various methods of gravity concentration have been employed, but the results usually show low metallurgical recovery and relatively high cost.

HEALTH HAZARDS

The health hazard surrounding operation of a quicksilver-reduction plant has been lessened to a great extent through the past 25 years. In furnaces of the old brickwork type, commonly operated on an undependable natural draft, leakage of fumes was not uncommon. The brick chamber condensers permitted the same conditions and, additionally, their cleanup was accomplished by actual entry of the cleanup crew into the chambers to sweep and hose them out. Not only the number of men in this crew, but the exposure to which they were subjected, caused frequent salivation, or mercurial poisoning, of very great incidence. With the development of mechanical furnaces and the present condensing systems, more attention has been given to this subject and salivation of operators has been reduced to a minimum. Compensation insurance rates applicable to plant operators is a tangible measure of the low hazard recognized for any modern installation.

In addition to improved mechanical design, which eliminates a large part of plant leakage and concentration of mercury vapor in plant areas, several devices have

been developed for the detection of mercury vapor in the atmosphere, thus making it possible to prevent unsafe conditions.

The General Electric Company's mercury detector utilizes a strip of paper coated with selenium sulphide, which, upon exposure to air carrying mercury vapor, turns brown. By comparison of color, the concentration may be estimated quite closely.

The development of an ultraviolet-ray absorption apparatus, by S. H. Williston, of Cordero mine, has provided a very accurate means of determining mercury-vapor concentrations of the atmosphere and plant gases, and also is used in ore analysis.

Other apparatus, reportedly utilizing a similar principle, is in the process of development but is not yet available for general use.

The occurrence of mercury vapor in some mines due to appreciable quantities of free quicksilver in the ore led to the development³ of a spray consisting primarily of a solution containing an alkaline polysulphide for the suppression of the mercury vapor. This solution, combined with appropriate spreader, adhesive, and other desirable additions, has been used to a certain extent not only in mines but also around furnace plants, with reportedly satisfactory results.

TYPICAL INSTALLATIONS

It may be interesting to note the general type of equipment used at several mines that have contributed a large part of the production of the United States and Canada during the past few years.

The largest plant in point of tonnage capacity and potential rate of production is that at the Pinchi Lake mine, British Columbia. This plant, reportedly of 1250 tons daily capacity, uses three eight-hearth Wedge furnaces, each 27 ft. in diameter, and two rotary furnaces, 4 ft. in diameter

by 60 ft. long, all arranged for wood and/or oil firing. Cyclone dust collectors and condensing systems are of cast iron, the rotaries utilizing 12-in. diameter pipe and the Wedges 16-in. diameter pipes. Dual exhaust fans in parallel are used on each furnace and at the end of the condensing system.

The New Idria mine, California, has the largest tonnage of any American plant, and for many years has been the largest American producer, ranking second to the New Almaden mine in total production of all North American mines. This plant, made up of four rotary furnaces 5 ft. in diameter by 56 ft. long, is the original successful rotary-furnace installation for reduction of quicksilver ore. During the past few years it has been remodeled, so that today it is one of the most efficient of American plants, although the furnaces are admittedly short for maximum capacity. The furnaces are followed by cyclone dust collectors, exhaust fans, 16-in. diameter cast-iron pipe condensing systems, redwood settling tanks and stackline to a single stack. Improved high-pressure oil firing with accurate draft control has very low oil consumption with maximum tonnage throughput and recovery.

The Hermes mine, Idaho, a newcomer to production, is equipped with two rotary furnaces of modern design, 4 ft. in diameter by 64 ft. long, and with other equipment as described above for the New Idria mine.

The Bonanza mine, Oregon, includes one 50-ton Herreshoff installation followed by a cyclone collector, condensing system including sheet-steel and vitrified-tile pipes, rubber-coated exhaust fan, settling tanks and stack. The rotary installation is the same as the Hermes mine.

The Cordero mine, Nevada, consists of a 14-ft. 3-in. diameter, 13-hearth Herreshoff three-zone furnace, previously described, followed by cyclone dust collector, condensing system including black-iron, cast-iron, and stainless-steel pipes, and thence

to rubber-coated exhaust fan, a settling tank and stack.

The Reed mine, California, includes a rotary kiln, 4 ft. in diameter and 60 ft. long, arranged for parallel flow of ore and gas stream, followed by cyclone collector, condensing system of 12-in. diameter cast-iron pipes, exhaust fan, settling tanks and stack.

Although other plants could be cited, these represent the more important mines and are representative of types of flowsheet used in nearly all plants from the smallest to the largest.

SUMMARY .

The modern mechanical furnace for the reduction of quicksilver ores is the result of about 27 years of development, during which time an almost complete transition has been made at North American mines from brickwork, manually operated furnaces, to continuous mechanical furnaces. The mechanical furnaces are of two principal types, the rotary and hearth furnaces, the former predominating by a rather wide margin. Little change from basic design of either type has taken place during this period other than mechanical improvements and application of better materials.

Dust-collecting equipment has been incorporated in all plants to rid the gas

stream of undesirable dust and thereby improve recovery and simplify quicksilver cleanup. The cyclone type is used almost universally.

Condensers, like the furnaces, have changed from large brickwork units to metal pipe systems, designed for greater efficiency, ease of cleanup and handling the product. Tile pipe is still occasionally used. Soot and mud, more often than not, are handled mechanically, improving recovery and reducing the incidence of salivation.

The metallurgical recovery of any well-designed modern plant, properly operated, should exceed 95 per cent, and should do so at operating costs averaging between \$1.50 and \$2.00 per ton.

Unlike the metallurgy of many other metals, that of quicksilver is fundamentally simple, and good results may regularly be obtained; common to all other metallurgy, standard equipment of a few types is the most satisfactory and careful operation with good supervision is essential.

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Reduction of Livingstonite Concentrate

BY H. B. MENARDI,* MEMBER A.I.M.E.

(Los Angeles Meeting, October, 1938)

THE history, geology, ore deposits and current mining operations of the Huitzuco district have been described by C. W. Vaupell¹ and the current mill operations by David Segura.² This paper completes the story of Huitzuco with a description of the reduction of the flotation concentrates.

The predominant ore mineral in the Huitzuco deposit is livingstonite, a rare, mercury-antimony sulphide ($\text{HgS} \cdot 2\text{Sb}_2\text{S}_3$). Other associated minerals include cinnabar, stibnite and elemental sulphur. The gangue is largely limestone and gypsum.

Former operators mined a selected grade of ore, from which the mercury was recovered by an expensive, inefficient operation. A considerable tonnage of rejects and fills, carrying mercury and antimony, was left in the mine. In order to recover both mercury and antimony from these fills and also from newly developed ore, a combination method has been developed, by means of which the livingstonite is concentrated by flotation and the flotation concentrates subsequently reduced to metallic mercury and antimony.

An essential part of the flotation treatment, as developed by Segura, is the use of copper sulphate as an activating agent. A typical analysis of concentrates now being produced at the property is as follows: Hg, 7.73 per cent; Sb, 26.40; Fe, 1.20; S, 29.68; CaO, 11.50; MgO, 7.25; SiO_2 , 1.63; Al_2O_3 , 0.65.

PROCESS FOR TREATMENT OF CONCENTRATES

In the development of a process for treatment of these concentrates, three different methods were investigated: (1) roasting in a Dwight-Lloyd sintering machine with an excess of air; (2) separation of mercury and antimony by distillation in a reducing atmosphere; (3) a third method, which ultimately developed into the present process. The third method involved a slow calcination at a closely regulated temperature with a limited admission of air, which separated the mercury and antimony, the mercury passing out of the kiln with the furnace gases and the antimony remaining in the calcine or "sinter."

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¹ C. W. Vaupell: A.I.M.E. *Tech. Pub.* 842 (*Min. Tech.* Sept. 1937).

² D. Segura: A.I.M.E. *Tech. Pub.* 896 (*Metals Tech.* Feb. 1938).

Laboratory results with the Dwight-Lloyd system indicated a clean separation of the antimony and mercury but it was thought that the excess of air involved would require an extensive condensing installation for recovery of mercury.

Experimental work on the separation of antimony and mercury by means of distillation in a reducing atmosphere showed interesting results by heating the first portion of the condensers. A clean, synthetic cinnabar product was recovered in the heated portion of the condensers and a clean sulphur product in the cool portion. This method was rejected because of indicated high labor costs and probable mechanical difficulties.

The third method, as finally adopted, involves a slow calcination under carefully controlled conditions of temperature and oxygen content. The oxygen is sufficient for burning only a portion of free sulphur in the concentrate and the temperature is just sufficient, under existing oxygen content, to split the livingstonite molecule into its component molecules of stibnite and cinnabar. The stibnite and unburned sulphur remain in the calcine or "sinter" while the vaporized cinnabar and carbon dioxide pass out of the furnace with the gases and into a special combustion chamber where the vaporized cinnabar is, in turn, oxidized or burned to metallic mercury (in vapor form) and carbon dioxide.

The calcine, or antimony "sinter," is withdrawn from the system and cooled without coming in contact with atmospheric oxygen, in order to prevent oxidation and fuming of the antimony. The subsequent smelting of this product will be described later.

In developing this process, laboratory experiments were made in an electric furnace, followed by tests on a larger scale in fixed retorts with hand rabbling. Final details were developed in a semicommercial installation, which included a rotary kiln.

PLANT OPERATIONS

Details of equipment and practice as finally developed at the Los Angeles plant, which has a capacity of approximately seven tons of concentrate per 24 hours, are shown in the accompanying flow diagram.

Concentrates are shipped from Mexico in box cars averaging 86,000 lb. wet weight. The concentrates are weighed and sampled in the transfer from box cars to storage shed.

From the storage shed, daily charge weights, samples and moisture determinations are made as the concentrate is fed into the treatment plant. Considerable difficulty was experienced in maintaining a uniform feed of concentrates into the kiln, until a combination arrangement of a belt feeder and water-cooled screw feeder was developed. With this combination it is possible to maintain a uniform, carefully controlled feed, which is essential to successful operation.

PRODUCTION OF MERCURY

Exit gases from the kiln, carrying volatilized cinnabar, sulphur vapor, sulphur dioxide and carbon dioxide, but no free oxygen, pass directly into the lower half of a combustion chamber. The upper half of the chamber contains a carefully arranged brick checkerwork and at the bottom there is an air opening with a regulating gate and a gas burner. An excess of air is admitted through the air opening and exit gases from the kiln burn with a peculiar blue flame on entering the chamber. The purpose of the checkerwork is to insure complete combustion. Three per cent free oxygen is maintained in the gases leaving the combustion chamber.

Gases from the combustion chamber pass through a cyclone dust collector and thence through a set of 11 steel condenser pipes in series, each pipe being 12 in. in diameter and 16 ft. high. These gases enter the steel condensers at 500° C. and are cooled to around 125° C. Each pipe is fitted with a steel condensing boot at the bottom, which collects metallic mercury and soot, or *cenicilla*, as it is called locally after the Mexican practice. These steel boots are luted on to the condenser pipe with mud and normally hold the product between general plant clean-ups, which are made about once each week. Recovery in the steel condensers normally accounts for 85 to 90 per cent of the recoverable mercury.

Following the steel condensers, the gas is passed through an exhaust fan and into three sets of 8-in. sewer-tile condensers operated in parallel. Water is sprayed into these tile condensers continuously and the bottom end of the pipe condensers dip into a shallow wooden tank. From the three parallel tile condensers the gases are passed through a wet cyclone collector and thence through two wooden tanks arranged with water sprays and baffles. Following these tanks is a second exhaust fan, which discharges into a wooden stack, which is 100 ft. high.

The two exhaust fans maintain a minus pressure throughout the system, so that all leakage is inward and any danger of mercury poisoning is eliminated.

The soot, or *cenicilla*, from the condensers is worked on a hoe table and retorted in the conventional manner. Mercury is packed in iron flasks holding 76 lb. 1 oz. net. Repeated determinations by well-known firms show that the finished mercury has a purity of 99.99 per cent plus.

PRODUCTION OF ANTIMONY

As described, the antimony sinter is withdrawn from the kiln and cooled so as to prevent oxidation of the antimony. A representative partial analysis of the sinter is as follows: Sb, 40.5 per cent; S, 20.8; Fe, 2.0; CaO, 9.0; MgO, 6.5; Al₂O₃, 1.0; SiO₂, 2.5.

The original program contemplated shipment of the antimony sinter to a custom antimony plant after the separation of the mercury, but the first commercial shipment from pilot-plant operations developed difficul-

ties on account of the lime-magnesia content and it became evident also that special refining treatment would be required. Therefore it was necessary to develop an economical, local treatment for production of competitive brands of antimony metal.

A series of leaching-electrolytic tests, using caustic soda and sodium sulphide, confirmed conclusions appearing in metallurgical literature; e.g., the electrolyte is not regenerated during electrolysis and the development of a satisfactory, insoluble anode material might present a very difficult problem.

Direct smelting of the sinter in a blast furnace was definitely eliminated because of the physical condition of the sinter, but several possible alternatives, using a reverberatory furnace, appeared to be feasible. In order to choose the best method, a large number of crucible melts were made, producing different types of slags, with varying combinations and fluxes, and with both roasted and raw sinter. From the results of these tests, fairly definite conclusions were reached:

1. The slag-forming requirements of the lime-magnesia constituents of the sinter were about the same in smelting raw and roasted sinter.

2. The silica-iron oxide-lime-magnesia slags acquired sufficient fluidity at reasonable operating temperatures.

3. High-silica slags are uniformly low in antimony.

4. In smelting raw sinter, sufficient iron must be provided to absorb the sulphur and form a matte.

5. Soda ash lowers the fusing temperature of the charge and also lowers the specific gravity of the matte.

6. The possibility of absorbing copper in the matte was indicated when smelting raw sinter and using metallic iron as a precipitant.

With these results available, a modified precipitation method was adopted, smelting the raw sinter direct and using cast-iron borings to displace the sulphur in the sinter and to regulate the fall of antimony metal. Iron oxide, as mill scale, is added to supply the iron requirements of the slag. Silica is charged in amounts to maintain the desired silicate degree. A limited amount of soda ash is used to help the slag and also to make a cleaner separation between matte and metal by lowering the specific gravity of the matte. An average charge consists of: 1000 lb. sinter, 200 lb. iron borings, 175 lb. silica, 100 lb. mill scale, 150 lb. soda ash.

In order to develop data for the design of an operating reverberatory, a small furnace, having a hearth 6 ft. long by 2 ft. wide, was erected. Based on the work in this furnace, a reverberatory with a hearth 16 ft. long and 5 ft. wide was erected to balance the mercury plant already in operation. The lining in this furnace is a good grade of firebrick, with magnesite brick at the slag line and around the flue opening. Charge is introduced from a hopper through two charge pipes on each side of the furnace at 4 and 7 ft. from the firing end. Charge and secondaries are

also shoveled into the furnace through doors in the burner end of the furnace. The flue is at the end opposite the burner. Metal, matte and slag are drawn together through a taphole in the side, near the flue end, into wheeled slag pots, each holding about 400 lb. The metal button is easily broken clean of matte and slag.

Gases pass out of the furnace through a small opening in the end, into a brick chamber which in turn is connected with a 42-in. diameter plate-steel flue 150 ft. long. The purpose of this flue is to cool the gases and collect the oxides. It is arranged in a loop and connects either with a two-compartment bag filter or through a by-pass to the exhaust fan which discharges either into a spray tower 6 ft. in diameter by 16 ft. high, filled with lattice work of round redwood poles, or directly into the stack through a by-pass.

FURNACE OPERATIONS

The daily flux mixture is varied to meet changes in the sinter feed. Conditions in the refining department are also a governing factor in the furnace operation.

The removal of copper from the finished metal is one of the refining problems. Oxides from the reverberatory furnace are practically free from copper provided the charge in the reverberatory is regulated so that not over 75 per cent of the antimony in the charge is fumed. An excess of metallic iron in the charge throws copper into the crude antimony metal rather than into the matte, therefore the balance between the mill scale and metallic iron requires careful control.

Normally the slag analysis is about as follows: SiO_2 , 36.7 per cent; FeO , 14.5; CaO , 19.6; MgO , 14.3; Na_2O , 3.5; Sb , 1.4. The amount of slag produced per ton of sinter averages about 950 lb. The antimony loss in the slag is 1.5 per cent.

Matte analysis is: Fe , 55.2 per cent; S , 33.7; Sb , 3.8; Cu , 0.85. The amount of matte produced per ton of sinter is about 735 lb. and the antimony loss is around 3.5 per cent.

Crude metal varies considerably in analysis, but generally is between 87 and 95 per cent Sb . The balance is largely Fe and other impurities are fairly constant at: Cu , 0.65 per cent; As , 0.31; S , 0.15; Pb , 0.05; Bi , nil; Sn , nil; Zn , nil. Copper in the sinter, although in very small quantity, goes both into the matte and into the metal, the distribution being governed by relative proportion of iron borings and mill scale used.

REFINING CRUDE ANTIMONY

The refinery department includes a "sweat" furnace, four small reverberatories for different stages in the removal of iron and arsenic and a tilting furnace for the preparation of the starring mixture. These furnaces are arranged in a straight line with connections to a header flue, and are served by a single track carrying mold cars along the tapping end.

The header flue with connections is 110 ft. long. It also is arranged in a loop and connects with the baghouse or by-passes to a second exhaust fan and thence either through the spray tower or directly to the stack in the same manner as the main header flue.

Two different types of finished antimony are produced in the refining department, one product being the crude metal from the reverberatory furnace, the other being oxides from the flues, baghouse and spray tower. These two products are kept separate throughout on account of the copper content of the reverberatory metal.

The crude metal from the reverberatory varies considerably in composition, particularly in iron content. If the iron content is high or if the crude metal generally is dirty, the metal is first put through the "sweat" furnace, which consists of a sloping hearth with a pool at the end. The antimony buttons are piled on the hearth and a slow fire is turned on, with just sufficient heat so that a fairly high grade of antimony metal melts or sweats out on this hearth and runs down into the pool, leaving a mass of dross and iron behind. Slag is skimmed from the pool through a door and the metal is tapped into molds.

For removal of iron this sweat metal is charged into a small reverberatory having a hearth area of 36 by 72 in. In this furnace either clean stibnite or sulphur is stirred into the molten charge in the calculated quantity to unite with the iron in the charge. Two side doors provide access for charging and slag skimming and metal is tapped into the molds in the same manner as the sweat furnace.

The next step in refining this product is the removal of the arsenic. Metal pigs are charged into the same type of furnace as is used for removal of iron and are melted with a slow fire. The addition of pigs is continued, with the skimming of slag and matte, until the furnace is filled with clean molten metal. The fire is then turned off and flake caustic is stirred into the molten metal with dry wooden poles. The quantity of caustic required is calculated from metal analyses. It is added in 25-lb. lots, with continuous poling between additions. If the metal appears to be cooling too rapidly, the fire is turned on for a short interval before each addition of caustic. Slag is skimmed after each addition and poling.

In the final step in the refinement of the metal, pigs are again heated in a small reverberatory with a small amount of soda ash, which forms a slag covering in the furnace. The metal is then tapped into molds. Just before the metal is poured, a measured quantity of a special "starring" mixture is poured into the mold. This mixture forms a skin between the metal and the mold also covers the top surface of the metal so that oxidation and contamination from the mold are entirely prevented.

REDUCTION OF OXIDES

The reduction of the oxides and flue dust is a simpler operation. The flue dust averages 75 per cent antimony and is treated in a small rever-

beratory with soda ash, charcoal and crude oil. The soda absorbs any small amount of sulphur, silica and antimony sulphide present and forms a thin layer of slag in the furnace, which prevents oxidation of the charge. The charcoal and crude oil from reducing agents for the production of metallic antimony.

Metal is tapped from this furnace and the pigs from this operation are treated for arsenic, as previously described.

FINISHED PRODUCTS

All finished metal has a clean, bright appearance and shows the characteristic stars of the trade. Finished pigs average between 42 and 43 lb. and are shipped either loose or in wooden boxes, as required by the trade. Three standard specifications are furnaces as follows: "C" Brand, 99.0 per cent antimony; "M" Brand, 99.5 per cent antimony; "M" Special, 99.8 per cent antimony.

The "C" Brand 99 per cent plus metal is the copper-bearing antimony from the reverberatory furnace. Impurities are 0.6 per cent copper, 0.05 per cent or less lead, iron, arsenic or sulphur.

The "M" Brand 99.5 per cent specification shows not more than 0.1 per cent of lead and not more than 0.05 arsenic, iron or sulphur.

The 99.8 per cent metal shows not more than 0.05 per cent of lead or of the other metals.

DISCUSSION

K. C. LI.*—The method described by the author for the production of antimony, using cast-iron borings to displace sulphur in the sinter and adding mill scale to supply the iron requirements of the slag, and the charging of silica to maintain the supply of desired silicate degree, is rather cumbersome, expensive, and involves too much labor, particularly when the smelting is to take place in America, where the labor cost is high.

The author described antimony metal as being produced in two stages: from the sinter to crude metal of about 87 to 95 per cent antimony and then from the crude metal to a metal of 99 per cent, containing about 0.6 per cent copper, which cannot be classified as good antimony metal.

From the analysis of the sinter, it seems that an oxidation or vaporization process along the lines that have been used by Chinese smelters would be very much cheaper and simpler, and

perhaps produce a better grade of metal. The sulphur in the sinter could be used as a self-combustion agent and no iron is necessary to displace it. Coke may be used to initiate the oxidation and frequently added to help it. A series of corrugated cast-iron, V-shaped but reversely erected, pipes or brick chambers with the maximum cooling surface may be used to allow the thorough precipitation of the oxide. In this way copper is eliminated. The antimony oxide thus precipitated can be reduced to antimony metal with charcoal and soda ash in a small reverberatory furnace, a small amount of flux being added to purify the metal before "starring" in the mold.

H. B. MENARDI (author's reply).—We made a number of experiments along the lines suggested by Mr. Li, and find that certain carloads of concentrates respond quite readily to the treatment he suggests while other carloads, although of approximately the same chemical analysis, are completely refractory to such treatment.

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Recovery of Precious Metals and Production of Selenium and Tellurium at Montreal East

By C. W. CLARK* AND J. H. SCHLOEN,† MEMBERS A.I.M.E.

(New York Meeting, February 1938)

Two papers have been written previously concerning operations at the Montreal East plant of Canadian Copper Refiners Limited. The first one,¹ written in 1932, described silver-refinery operations at the time for producing silver and gold bullion from tankhouse anode slimes; the second,² published in 1933, consisted of a description of the entire plant. Since publication of these papers the refinery has become the world's largest producer of refined selenium. The first selenium was produced in August 1934. Tellurium production on a commercial scale followed in October 1935. This paper will deal with selenium and tellurium production and also with present operations in the silver refinery.

Blister cakes from Hudson Bay Mining and Smelting Co., Flin Flon, Manitoba, and commercial anodes from Noranda Mines Limited, Noranda, Quebec, are refined at Montreal East. Both these bullions have unusually high gold, selenium and tellurium content. The average assay of raw slimes produced from domestic and Noranda anodes is about 40 per cent Cu, 3600 oz. per ton Ag, 800 oz. per ton Au, 22 per cent Se and 3.7 per cent Te.

EARLY SILVER-REFINERY OPERATIONS

From the start of operations in 1931 until July 1934, the raw slimes were oxidize-roasted at 700° F. in a Nichols-Herreshoff furnace, acid-leached with tankhouse discarded foul electrolyte (20 per cent H₂SO₄), filtered and charged directly to the doré furnace for refining to doré metal.

This is the customary method for treating tankhouse anode slimes but was not suitable at the Montreal East plant because of the high selenium and tellurium content of our slimes.

In the acid-leaching process about 50 per cent of the selenium and tellurium in the roasted slimes was dissolved in the electrolyte. These elements were recovered with the copper as a sludge in a small electrolytic

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¹ C. W. Clark and A. A. Heimrod: *Trans. Electrochem. Soc.* (1932) 61.

² H. S. McKnight: *Trans. A.I.M.E.* (1933) 106.

purification system, which used lead cathodes and lead anodes. Lead cathodes were necessary because copper cathodes redissolved in the electrolyte and cemented selenium and tellurium from the solution. After electrolytic deposition the leach liquor was passed over scrap iron to recover the remaining copper, selenium and tellurium as a cementation mud, which was re-treated in the copper-anode furnace. The deposit from the purification system contained about 45 per cent Cu, 35 per cent Se and 6 per cent Te, and was known as "liberator mud." This mud was stored and now is being re-treated for recovery of metal.

The selenium and tellurium remaining in the acid-leached slimes were eliminated from the plant cycle by discard of doré-furnace soda-slag leach liquors and doré scrubber-system solutions.

For a short time in 1931 the oxidized, or roasted, slimes were treated with caustic potash solutions prior to acid leaching to eliminate selenium and tellurium from the slimes as potassium selenites and tellurites. This step was discarded from the original silver-refinery flowsheet, for two reasons: (1) poor selenium and tellurium elimination and consequent high cost of caustic per pound of selenium eliminated; (2) difficulty in filtering the caustic-leached slimes.

To summarize, prior to August 1934, selenium and tellurium were eliminated from the refinery cycle at five points in the flowsheet:

1. In caustic-leach liquors from treating roasted slimes. This was an outlet for a short time only.
2. In doré-furnace soda-slag leach solutions to sewer.
3. In scrubber solutions to sewer.
4. In cementation liquors to sewer.
5. In liberator mud, which was recovered and stored for re-treatment.

PRESENT SILVER-REFINERY OPERATIONS

The present processing of tankhouse slimes can be divided into eight steps as follows (Figs. 1 and 2):

1. Drying and roasting slimes with sulphuric acid for selenium elimination and conversion of metallic and oxide copper to water-soluble sulphate.
2. Water leaching of roasted slimes to remove soluble copper.
3. Caustic-soda leaching of water-leached slimes to remove tellurium.
4. Refining of caustic-leached slimes to doré bullion.
5. Separation of gold and silver by Moebius system.
6. Production and refining of selenium.
7. Production and refining of tellurium.
8. Recovery of acid from slimes water-leach liquors and discarded tankhouse electrolyte.

Raw slimes are pumped from the tankhouse to the silver-refinery surge tank, from which they are delivered at a uniform rate by Dorrey

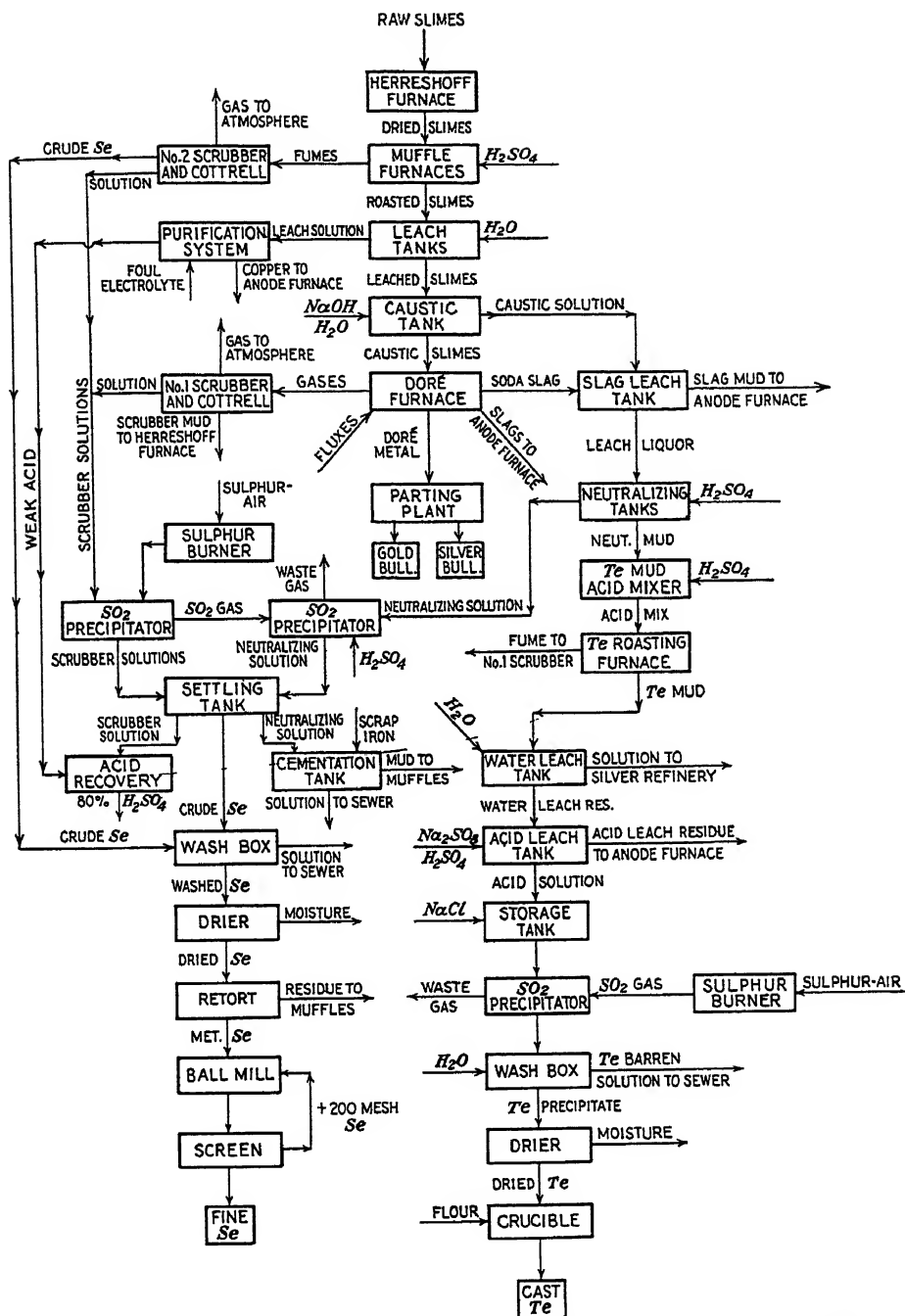


FIG. 1.—FLOWSHEET OF SILVER REFINERY WITH SELENIUM AND TELLURIUM DEPARTMENTS.

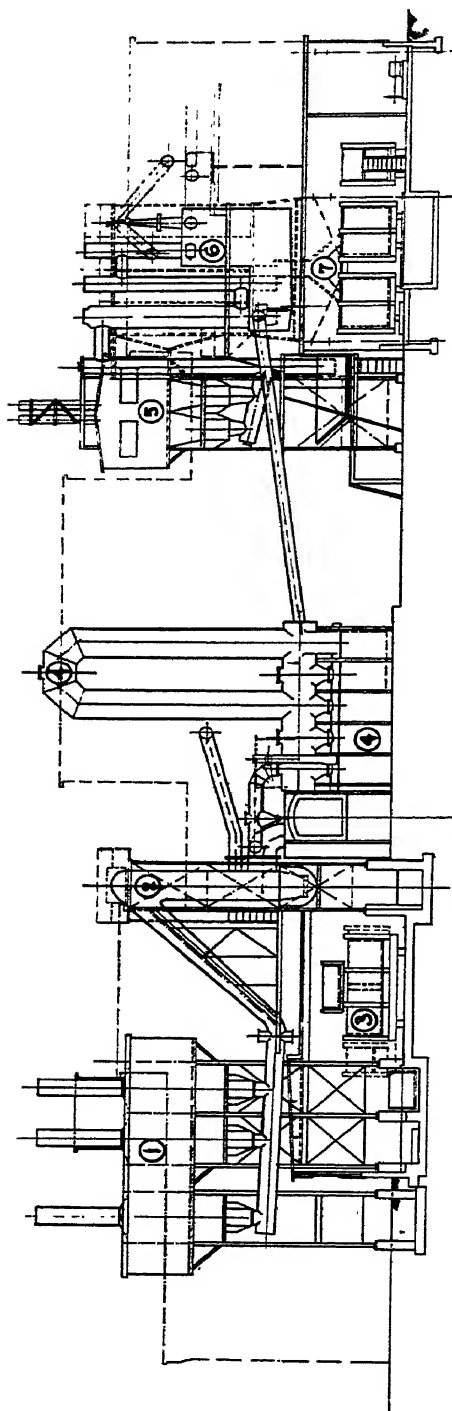


FIG. 2.—SECTION OF EASTERN SIDE OF SILVER REFINERY.

1. No. 1 Cottrell precipitator.
2. No. 1 scrubber system for doré furnace gases.
3. No. 1 scrubber-solution settling tanks.
4. Doré furnace flue system.
5. No. 2 Cottrell precipitator.
6. No. 2 scrubber system for muffle-furnace fumes.
7. No. 2 scrubber-solution settling tanks.

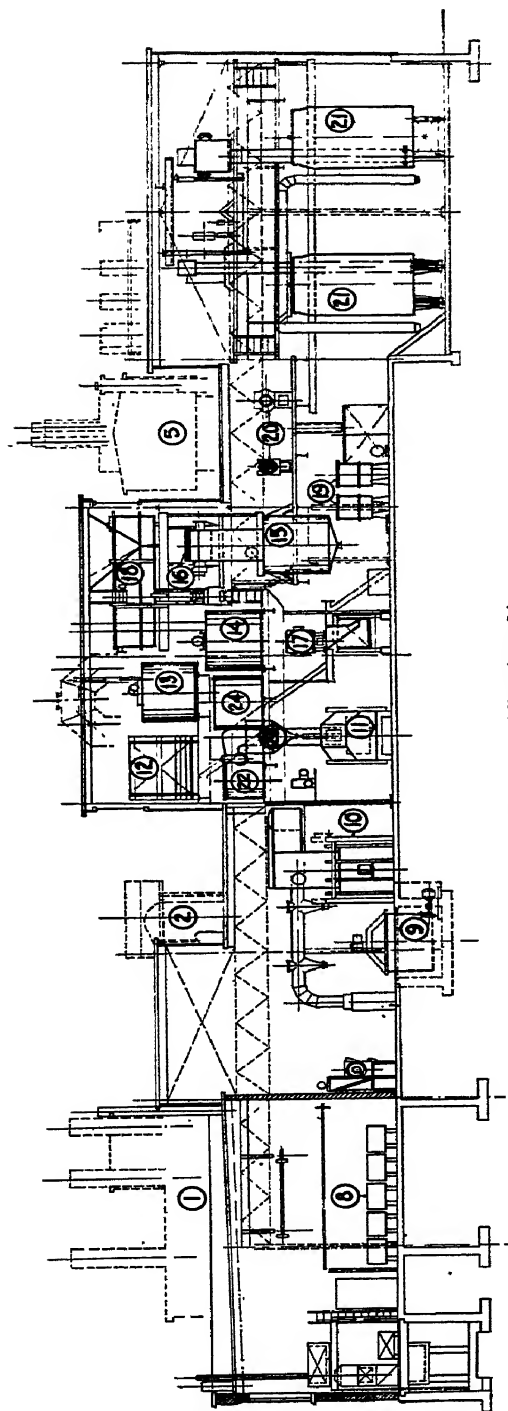


Fig. 2.—(Continued.)

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|--|---|
| 8. Moebius cells in parting plant. | 17. Filter press for caustic-leached slimes. |
| 9. Soda-slag leach tank. | 18. Storage tank for caustic leach solution. |
| 10. Doré furnace. | 19. Caustic-leach filtrate tanks. |
| 11. Furnace for roasting tellurium mud. | 20. Filter presses for scrubber mud and slag leach mud. |
| 12. Storage tanks for slimes water-leach solution. | 21. Muffle furnaces |
| 13. Slimes water-leach tanks. | 22. Wash-water storage, parting plant. |
| 14. Holding tanks for water-leached slimes. | 23. Tellurium mud-acid mixer. |
| 15. Slimes caustic-leach tank. | 24. Scrubber-solution storage. |
| 16. Oliver continuous filter for water-leached slimes. | |

diaphragm pump to a 10-ft. diameter Dorr thickener. The thickened slimes are discharged from the thickener to a 3 by 4-ft. Oliver continuous filter. The thickener overflow and Oliver filtrate are returned to the tankhouse storage tanks from a settling tank in the silver refinery.

The filtered slimes, containing 25 to 30 per cent moisture, discharge from the filter directly to the top hearth of an 8-ft. diameter six-hearth Nichols-Herreshoff furnace. The furnace dries the slimes at 250° to 300° F. down to 10 per cent moisture only. This moisture helps to prevent dusting during subsequent handling, which is an important consideration in treating such high-grade material.

The heating medium on the Nichols-Herreshoff furnace is bunker C fuel oil fired in a Dutch oven. Combustion gases from the furnace are exhausted to doré furnace flue and scrubber system.

Acid Roasting of Slimes

The Nichols-Herreshoff furnace discharge, known as dried slimes, is hoisted to the muffle-furnace platform, where the slime is mixed mechanically with about 75 per cent its weight of 60° Bé. recovered sulphuric acid before it is fed to the roasting furnaces. Certain silver-refinery and selenium-plant by-products, such as flue dust, scrubber mud and retort residue, are also acid-roasted in the muffle furnaces. The purpose of acid roasting is twofold: (1) from 80 to 95 per cent of the selenium content of the furnace feed is volatilized to the scrubber system; (2) 95 per cent of the copper content is converted to water-soluble sulphate for removal by water leaching.

There are two muffle furnaces of essentially the same design (Fig. 3). Each is of cast-iron construction, 8 ft. 0 in. in diameter, with eight roasting hearths, an equal number of combustion hearths and a top drying hearth. The furnaces are of the split type, to facilitate major repairs. All hearth connections to combustion-gas manifolds and acid-fumes manifolds are made on the stationary halves of the furnaces. There are three inspection doors on each roasting hearth and one on each combustion hearth. The roasting-hearth doors are large enough to pass a rabble arm fitted with teeth. Rabble teeth on acid hearths are made of stainless steel, while those on all other hearths are made of cast iron.

In addition to the acid mixed with the dried slimes before they are charged to the furnaces, acid is added through sprays on the third and fifth roasting hearths. In all, 2.2 to 2.5 lb. 60° Bé. sulphuric acid is used per pound of dried slimes.

The heating of the furnaces is accomplished by four 1¼-in. diameter burners set radially 90° apart on each combustion hearth. Vaporized light fuel oil, produced by a No. 9 Vapofier for each furnace, is fired through these burners. Both furnaces are lagged with 2 in. of Eagle No. 66 insulating cement. Roasting temperatures are maintained at

700° to 800° F. A permanent record of individual hearth temperatures is kept on Foxboro multipoint recorders.

The furnace shafts make one revolution every 50 sec. At this shaft speed the average roasting time for slimes is approximately 3 hr. The

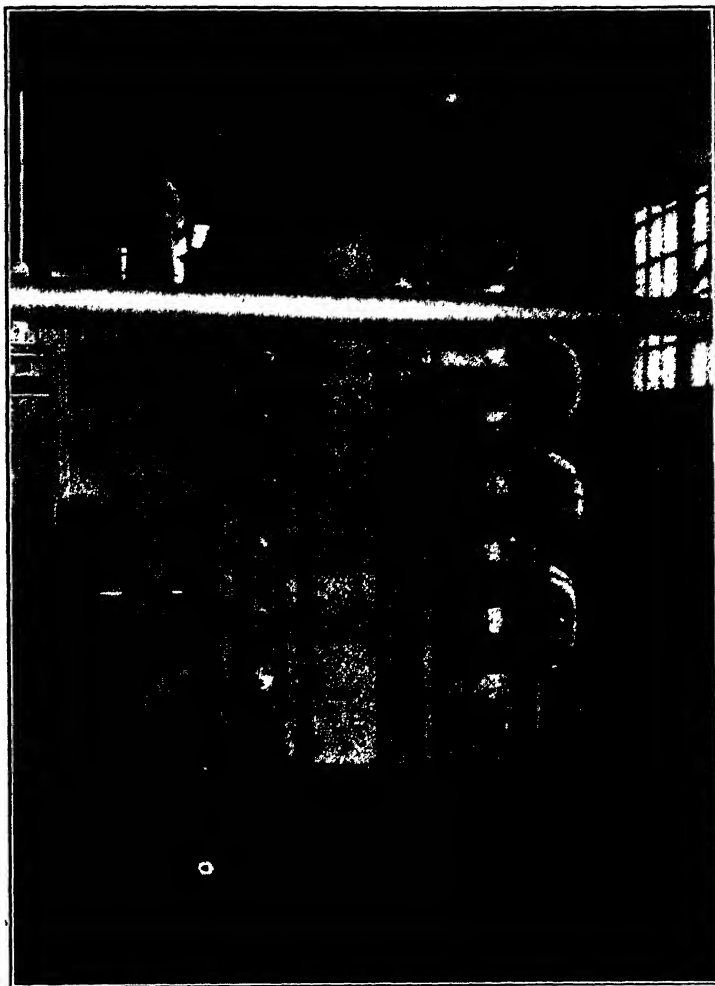


FIG. 3.—No. 2 MUFFLE FURNACE, SHOWING COMBUSTION GAS MANIFOLD AND TWO SETS OF SLIMES HEARTH INSPECTION DOORS. TEMPERATURE RECORDERS IN BACKGROUND.

combined production from the two muffle furnaces is 205,000 lb. of roasted slimes per month.

The furnaces are built on the muffle principle, combustion gases and acid fumes being handled separately. The combustion gases are exhausted by fan to the doré furnace flue and scrubber system as an insurance against possible metal loss.

Selenium Scrubber System

The acid fumes and gases from the roasting hearths of the muffle furnace are drawn through a lead-lined fumes manifold, where they are cooled with circulating scrubber solution. The cooled gases are exhausted by Corrosiron fan to a four-tower scrubber system. Each tower is equipped with lead sprays supplied with scrubber solution, which circulates through the towers, scrubber seal (or "bathtub"), settling tanks, pump tank and return. The scrubber system conditions the gas prior to Cottrell precipitation and, in addition, recovers the greater part of the selenium, selenium dioxide and acid content of the gas. A total volume of approximately 800 gal. per min. is supplied by six centrifugal pumps to the rain plates of the fumes manifold and the scrubber-tower sprays.

The products from the scrubber system are crude selenium and scrubber solution. Crude selenium is cleaned from the system daily. Scrubber solution is treated for selenium only when the selenium content has built up to one pound per cubic foot of solution. Both crude selenium and scrubber solution are treated in the selenium plant as explained later.

The Cottrell treater consists of two pipe units in parallel. Each unit has eight 8-in. diameter pipes and one 11-in. diameter pipe with the stiffener electrode. The entire Cottrell and scrubber system is constructed of lead and lead-covered steel, to resist the acid content of the gases being treated. The Cottrell treats 1800 cu. ft. per min. at 95° F., with an average daily stack loss of 2 lb. of selenium.

Both units of the Cottrell are cleaned down three times daily, once on each shift. Selenium collected in the Cottrell is processed in the same way as selenium from the scrubber system.

Water Leaching of Roasted Slimes

Roasted slimes discharged from the muffle furnaces assay about as follows: total Cu, 26 per cent; water-insoluble Cu, 1 per cent; Se, 3 per cent; Te, 2.4 per cent; Ag, 2340 oz. per ton; Au, 520 oz. per ton. This assay indicates an 80 per cent elimination of selenium during roasting. Actually, when straight slimes are handled through the muffle furnaces, 95 per cent Se eliminations are common, but this figure is considerably lower when residues of high selenium content are re-treated in furnaces.

The roasted slimes are hoisted, in buggies containing 1200 lb., to the leach-tank platform for charging in 3500-lb. batches to the lead-lined tanks. A counter-current system of leaching and decantation is employed. Second and third leach liquors from the previous batch are used for first and second leaching, respectively. Fresh water is used for final leaching. Direct steam is used for heating. No acid is used in

the leaching. If the leach liquor shows silver in solution, this is precipitated in leach tanks by means of copper scale from wire mill or high copper residues from the tankhouse. Excess copper additions are guarded against.

First leach liquors are decanted through a filter box to the purification system for copper recovery and acid regeneration. The weak acid from the purification cells is sent to the acid-recovery system for concentration to 60° Bé. prior to re-use in muffle furnaces.

At the conclusion of decantation of the third leach liquor, the water-leached slime is discharged from the leach tank to a holding tank. After four leached batches are accumulated in this tank the leached slimes are fed at a uniform rate by Dorco diaphragm pump to a 3 by 4-ft. Oliver continuous vacuum filter. The Oliver filtrate is pumped back to water-leach liquor-storage tank for use in subsequent leaches.

There is approximately 80 per cent reduction in the weight of roasted slimes during the leaching process, so that the grade of water-leached slimes is about as follows: Cu, 4 per cent; Ag, 11,700 oz. per ton; Au, 2600 oz. per ton; Se, 15 per cent; Te, 11 per cent.

Caustic Leaching of Slimes

The leached slime is discharged from the Oliver filter directly into the caustic treatment tank, which contains 150 cu. ft. of 10 per cent caustic soda solution. The purpose of this caustic leach is to remove the greater portion of the tellurium content of the leached slimes and thereby reduce the doré-furnace flue products—dusts and scrubber mud. About 85 per cent of the tellurium is removed by the caustic treatment.

At the conclusion of the leach the slimes and liquor are pumped through a 28-plate, 36 by 36-in. Shriver iron-plate filter press of the open discharge type. Two filtrate tanks are provided. Filtrate is run to the first tank until the solution is completely clear. This first filtrate is siphoned back to the caustic-treatment tank. The clear filtrate runs to the second tank, from which it is pumped to storage. As required, this caustic solution is used for leaching doré soda slags. In this way two sources of selenium and tellurium are combined and an appreciable reduction in volumes to be handled is effected. The caustic-leached slimes are retained in the filter press until they have been well washed with hot water, this water being returned to caustic-treatment tank to be used as make-up for the following batch. After washing, the slimes are blown with compressed air to aid moisture removal and are then dumped to a furnace buggy.

Caustic-leached slimes are handled in 3500-lb. batches containing 30 per cent H₂O and assaying: Cu, 4 per cent; Ag, 12,000 oz. per ton; Au, 2700 oz. per ton; Se, 14 per cent; Te, 1.5 per cent.

It is to be understood that all analyses given up to this point are to be taken as present averages and will, naturally, vary with the grade of material received at the refinery.

Caustic-leached slimes are charged to the doré furnace for refining to metal for Moebius-cell parting.

Doré-furnace Practice

The doré furnace is built on the reverberatory type and is fired with bunker C fuel oil. The hearth is built of 12-in. Lofero magnesite brick in the form of an inverted arch with a spring of $4\frac{15}{16}$ in. The hearth bricks were soaked in light fuel oil and set in a mortar of Lofero cement and fuel oil. This type of hearth absorbs much less metal than either the ordinary burned or unburned magnesite. The hearth area is $34\frac{1}{2}$ sq. ft. Under the hearth is set $2\frac{1}{2}$ in. of firebrick, a $\frac{1}{2}$ -in. steel plate and 4 in. of concrete, all of which is supported by 2 by 6-in. channels resting on concrete piers 12 in. above floor level.

The furnace side walls up to 1 ft. $10\frac{1}{4}$ in. above the hearth are constructed of 12-in. Lofero magnesite brick similar to the hearth. The upper side walls are made of fire-clay brick. The furnace roof is built of fire-clay brick and is 6 ft. 8 in. above floor level at the burner end and 5 ft. 0 in. above floor level at verb. The verb is constructed of steel-cased unburned magnesite brick supported on stainless-steel hangers, which rest on a water-cooled pipe. The bridge wall of the furnace is faced with a $4\frac{1}{2}$ -in. course of carborundum brick. The uptake, which has an area of $5\frac{1}{2}$ sq. ft., is built of steel-cased unburned magnesite brick at its lower end.

The furnace is charged through a door in the side wall and is skimmed from the front. A charge consisting of 10,000 to 12,000 lb. of slimes, containing 30 per cent moisture, is well mixed with fine soda and silica before charging. This mixture is charged to the doré furnace in 500-lb. additions. Besides the slimes, certain silver-refinery by-products are also charged to the doré furnace, and the furnace is then sealed. When the charge is completely molten the furnace is opened and the No. 1, or scoria, slag is skimmed off. This slag, which contains most of the lead, arsenic, antimony and iron, is crushed and returned to the copper-anode furnace.

(In passing, we may say, because of the high grade of material being treated and the lack of a secondaries smelting furnace in the plant, we are forced to re-treat a large tonnage of by-products in the anode furnace.)

The doré charge is next blown with air, fused soda ash being used for a flux. The soda slag formed contains most of the selenium and tellurium from the charge. This slag is leached with caustic liquor from the slimes treatment. The residue from the slag leach is returned to the anode furnace, while the filtrate is treated for recovery of selenium

TABLE 1.—*Typical Log of a Doré Furnace*

Operation	Elapsed Time, Hr.	
	Without Iron	With Iron
Charging.....	15 7	15.7
Melting.....	6.7	6.7
Skimming No. 1 slag.....	1.5	1.5
Blowing with soda and skimming soda slag.....	17.0	} 18.8
Refining with niter and skimming copper slag.....	11.4	
Casting.....	3.6	3.6
Total time.....	55.9	46.3

Fluxes Used	Pounds	
Soda.....	852	852
Purite.....	2,590	1,650
Niter.....	2,450	1,460
Silica.....	410	410
Scrap iron.....	0	800

Slag Produced	Pounds
No. 1 slag.....	4,740
No. 2 slag.....	3,890
Copper slag.....	2,740

Metal Produced	Troy Ounces
Doré metal.....	46,429
Silver content of doré.....	38,129
Gold content of doré.....	7,654

Typical Analyses for Doré-furnace Products

	Cu, Per Cent	Ag, Oz. per Ton	Au, Oz. per Ton	Se, Per Cent	Te, Per Cent
No. 1 slag.....	1.43	170	17.6	0.75	0.52
No. 2 slag.....	2.45	264	7.8	17.51	5.72
Copper slag.....	16.00	1300	25.1	6.15	0.50
Flue dust.....	5.71	810	120.1	32.06	2.55
Scrubber mud.....	0.40	1049	43.2	28.82	0.91

and tellurium. Recently scrap iron has been used in addition to the soda for breaking down the selenium matte into bullion and soda slag. When iron is used no blowing is required. The iron addition has materially reduced the amount of chemicals required per ounce of doré metal produced and the time required to process a charge through the furnace. About 40 per cent of the former chemical cost is saved and 10 hr. are cut off each furnace charge. No new iron is bought for fluxing, as sufficient scrap rabble teeth and similar material is always available in the silver refinery.

The final stage of furnace refining is the removal of the copper content by rabbling the charge with niter. The copper slag skimmed off is crushed and returned to the anode furnace for re-treatment.

Just prior to casting, the doré metal is cleaned up with Portland cement. The slag from this cleaning is recharged to the furnace with subsequent charge. The doré metal is ladled into water-cooled molds by hand. Anodes are 6 by 9 by $\frac{1}{2}$ in., weigh approximately 150 Troy ounces each and assay 845 parts fine silver, 150 parts fine gold and 5 parts copper. The average production of the doré furnace is 45,000 Troy ounces per charge, or 225,000 oz. per month. A typical doré furnace log, for a charge of 10,000 lb. of wet caustic-leached slimes (30 per cent H_2O) and 2000 to 3000 lb. of sundry material such as return slag, is given in Table 1. The effect of iron addition during the soda-slag period is clearly shown.

Doré-furnace Flue, Scrubber and Cottrell System

The gases leave the doré furnace at 2500° F. and pass through a brick flue and a steel flue for cooling and removal of considerable flue dust. The gases then pass through the exhaust fan and enter the scrubber system at 400° F. In addition to the doré-furnace gases, all gases from the Herreshoff furnace, tellurium-mud roasting furnace and combustion hearths of muffle furnaces are also exhausted through the scrubber system for conditioning prior to Cottrell precipitation.

In passing through the three-tower scrubber system, the gases are completely saturated with water by sprays and rain plates and about 90 per cent of the remaining dust is precipitated as a scrubber mud. A total volume of approximately 450 gal. per min. is supplied by three centrifugal pumps to the doré-furnace scrubber-tower rain plates and sprays. Scrubber mud and solution is filtered through a 24 by 24-in. Sperry lead-plate filter press. The mud is returned to the Nichols-Herreshoff furnace for re-treatment. The scrubber solution is pumped to the selenium plant for recovery of selenium and acid.

The gases leave the scrubber at 125° F. and pass to a three-unit Cottrell precipitator of the pipe type. Each unit consists of eighteen 8-in. diameter pipes and two 11-in. diameter pipes, all 12 ft. long. The

entire precipitator and scrubber system is constructed of antimonial lead and lead-covered steel.

Each Cottrell unit has a damper for control of gas volume and a switch for cutting the unit out of circuit for maintenance and repair. The pipes are cleaned with a scraper at the end of each doré charge and the alignment of electrodes is checked at the same time. The Cottrell handles a total gas volume of 8000 cu. ft. per min. at 95° F., the average daily metal losses from the Cottrell stacks being: 1.5 oz. Ag, 0.027 oz. Au, 1.7 lb. Se, 0.2 lb. Te. Continuous 24-hr. sampling tests are run on gases from this Cottrell as well as on the muffle-furnace Cottrell.

Power for Cottrells

Incoming power from the Montreal Light, Heat & Power Consolidated is supplied at 12,000 volts, three phase, 60 cycles. This voltage is stepped down to 550 volts and then by means of a 15-kva. transformer is boosted to 45,000 to 65,000 volts. This high-voltage current is rectified by a synchronously driven mechanical rectifier. The unidirectional current is supplied to the Cottrell units. Voltage on the precipitators is controlled in three ways: (1) low-voltage rheostat on primary side of incoming alternating current; (2) high-voltage resistance; (3) taps on high-voltage transformer. There are two complete rectifier units in the main powerhouse. The two rectifiers are arranged so that either or both can be used on either or both of the Cottrells. This provides complete flexibility of control. A private telephone system connects both Cottrell units with the powerhouse.

Parting Plant

The anodes from the doré furnace are taken to the parting plant for parting into silver and gold by the Moebius system. There are 10 rubber-lined concrete Moebius cells arranged in two groups of five cells each. The cells measure 2 ft. 5½ in. by 2 ft. 9½ in. by 1 ft. 10¾ in. inside rubber lining. Fifteen doré anodes are suspended in each cell, so that 150 anodes, weighing approximately 22,000 Troy ounces, are contained in the newly loaded cells.

The electrolyte in the cells at present assays: Ag, 50 grams per liter; Cu, 15 grams per liter; and free HNO₃, 2 grams per liter.

There are two motor-generator sets in the powerhouse, each one supplying the current for one set of five Moebius cells. The average power requirements for five cells is 13 volts and 475 amp. Since the cells are in series, with the anodes and cathodes in each cell in parallel, the current density is 28 amp. per sq. ft. of cathode area. Each set of three anodes in parallel is enclosed in a filter duck bag, to retain the gold residue from the electrolytic deposition of silver crystals on rolled silver

cathodes. Cathodes when new measure 12 by 20 by $\frac{1}{16}$ in. thick. Bakelite is used for the gold-bag frames.

In each cell is suspended a wooden frame basket having a filter-cloth bottom. Continually reciprocating wooden scrapers brush the silver crystals from the cathodes into the basket filter bottom. The baskets are withdrawn from the cells once every 24 hr. for removal of the silver crystals. These silver crystals are washed with water in a filter-bottom stoneware cart, to remove all traces of electrolyte. The silver sand is dried and melted in a graphite retort, 14,000 oz. at a time. Silver bullion is cast in bars weighing 1000 Troy ounces and assaying 999+ fine.

The average life of 150-oz. anodes containing 15 per cent gold is 36 hr. When necessary, scrappy anodes are replaced in cells by new ones. Once every four days all anodes are removed from the cells and scraped. The gold mud from the anodes is combined with that from the filter bags, washed with water and leached with boiling concentrated sulphuric acid, to remove most of the silver. After being leached, the gold sand is washed well with water and drained on filtros blocks. The sand is melted in a graphite crucible and cast into bars weighing 750 Troy ounces each and assaying 995+ fine gold. Gold bullion is shipped directly to the Royal Canadian Mint at Ottawa.

Anode scrap, after being scraped clean, is remelted in a graphite crucible and cast into doré anodes for parting. With anodes assaying 150 parts fine gold, the weight of scrap averages about 12 per cent of the loading.

Silver from all parting-plant wash solutions and gold-boiling acids is recovered by cementation with scrap copper and is re-treated in the doré furnace or used for make-up material for parting-plant electrolyte.

SELENIUM PLANT

The selenium, tellurium and acid-recovery departments are in a 60 by 60-ft. self-contained building, about 200 ft. from the silver refinery. The building is composed of three 20 by 60-ft. bays. As far as possible each of the three departments is built entirely within one bay, to facilitate handling materials and to minimize contamination of refined products.

Three classes of material are received at the selenium plant for processing: crude selenium from the muffle-furnace scrubber, neutralized

TABLE 2.—*Typical Assays of Materials Received at Selenium Plant*

Materials	Se, Grams per Liter	Te, Grams per Liter	H ₂ SO ₄ , Grams per Liter
Doré scrubber solution.....	45	4.50	180
Muffle-furnace scrubber solution.....	18	0.15	200
Neutralized slag-leach solution.....	20	0.25	0
Crude selenium, per cent.....	97.5		

slag-leach solution and scrubber solutions. Typical assays of the three materials are given in Table 2.

Precipitation of Selenium from Scrubber Solutions

All solutions are pumped from the silver refinery through an underground tunnel to the storage tanks at the selenium plant. Solutions are drawn from storage to the precipitators as required.

The precipitation of selenium from selenious acid solutions is based on this equation:



which shows that for every pound of selenium precipitated approximately $2\frac{1}{2}$ lb. of sulphuric acid is generated.

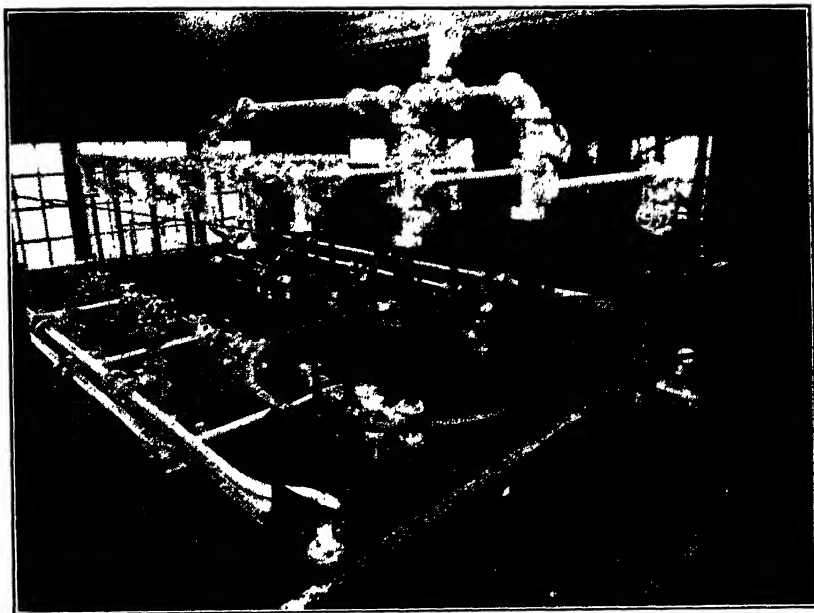


FIG. 4.—SULPHUR DIOXIDE PRECIPITATORS.

The precipitators (Fig. 4), of which there are six in series, are lead-lined dished-end tanks, 5 ft. 0 in. in diameter by 8 ft. 6 in. high. Each precipitator has an inlet and an outlet for sulphur dioxide gas, an outlet for waste gas, a manhole for inspection, a solution inlet and a bottom discharge for solutions after precipitation is complete. Besides, a thermometer, pressure gauge and sampling cock are provided on each precipitator for control purposes. Each precipitator has a cooling coil to maintain the temperature of the solution between 60° and 90° F. during precipitation. Above 100° F., selenium precipitates become

plastic and are difficult to clean from the precipitator, while below 60° F. too great a quantity of sulphur dioxide gas is required to saturate the solution.

The six precipitators are connected in series in a closed circuit, so that, by means of valves, any one of the six tanks can be the first one in series or can be removed from the circuit at any time. Series precipitation under pressure aids greatly in securing effective recovery of selenium with the minimum amount of sulphur dioxide gas. At the refinery, for every pound of sulphur burned an equal amount of selenium is precipitated, which indicates an efficiency of 80 per cent according to the

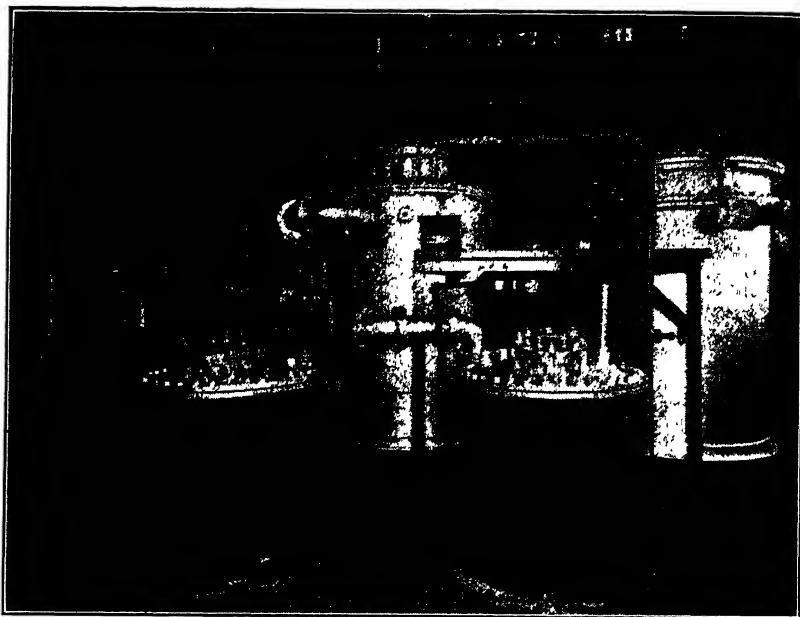


FIG. 5.—EQUIPMENT FOR GENERATING SULPHUR DIOXIDE GAS.

equation given above. This figure is possible only if four or more of the six precipitators are in service all the time.

The time required for precipitation varies directly with the concentration of selenium in the solution treated, the average being about 5 hr. per tank. When a sample from a precipitator shows completion of precipitation, that tank is cut out of circuit. The precipitator is vented carefully to remove excess sulphur dioxide, after which the manhole cover is removed and the spent solution with selenium precipitate is washed through the bottom discharge to the settling tank.

In the settling tank the solutions are boiled to remove the last traces of sulphur dioxide gas. The selenium is allowed to settle, after which the solution is decanted and pumped to the acid-recovery storage tanks.

It is impossible to precipitate selenium completely from straight sulphuric acid solutions, so that spent scrubber solution assays about 0.5 gram per liter Se and 0.2 gram per liter Te. Most of this selenium is recirculated in the acid produced from concentrating these spent solutions.

The crude selenium from the settling tank is washed with water through a $\frac{1}{4}$ -in. screen and is filtered in a vacuum wash box. From this point in the selenium process all materials entering the plant are treated alike.

Precipitation of Selenium from Neutral Slag-leach Solutions

Neutral slag-leach solutions are acidified with 10 per cent their weight of 66° Bé. sulphuric acid before they are gassed with sulphur dioxide. As regards the actual precipitation, the same procedure is followed for scrubber solutions and neutral slag-leach solutions, but the disposal of the spent solutions is different.

Because of their high content of sodium salt, spent slag-leach solutions cannot be treated for acid recovery. These solutions, after being boiled in the settling tank for removal of sulphur dioxide, are pumped to a cementation tank, where a considerable amount of the selenium is recovered on scrap iron before the solution is discarded to sewer.

Of the total selenium production, about 50 per cent comes directly from muffle-furnace scrubber crude selenium; the remaining 50 per cent comes from precipitation of scrubber solution and neutral slag solutions.

Generation of Sulphur Dioxide Gas

The sulphur dioxide gas is generated by burning elemental sulphur in a water-jacketed brick-lined steel tank, 2 ft. 9 in. in diameter by 3 ft. 2 in. high. Air under pressure is introduced above the surface of the molten sulphur. The burner with six precipitators in circuit operates at a pressure of 20 lb. per sq. in. and a temperature of 400° F. Under these conditions it is possible to burn 20 lb. of sulphur per hour, which will precipitate an equal weight of selenium. (Fig. 5.)

The gas discharges from the sulphur burner into a steel expansion tank 4 ft. 0. in. in diameter by 6 ft. 0 in. high. The purpose of this tank is to settle elemental sulphur sublimed over from the burner and to cool gases to 250° F. before they pass on to a lead-lined water scrubber tank of the same size as the expansion tank.

Sulphur dioxide gas passes from the scrubber at 17 lb. per sq. in. and 100° F. to the first precipitator in series on the floor above.

Refining Crude Selenium

After the crude selenium is washed in the filter box, it is dried in an oven.

Crude selenium assays from 0.01 to 0.30 per cent Te, depending on the source of the material. Charges of 1000 lb. to retorts are blended so that the average grade is 0.10 per cent Te.

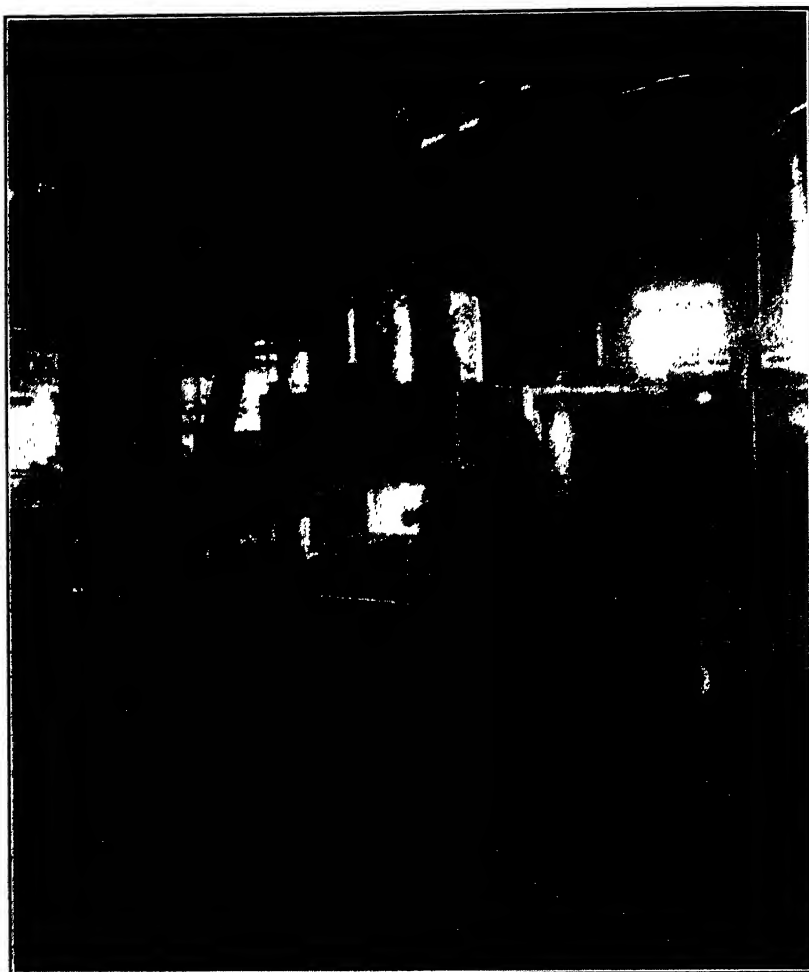


FIG. 6.—SELENIUM RETORT IN OPERATION.

Retorting crude selenium serves two purposes: it reduces the tellurium content to less than 0.10 per cent and it recovers in the residue any silver and gold that may have been in the crude selenium.

The retort bowls are made in gooseneck style of cast iron. Retort covers are made of cast iron containing 1 per cent Ni. After every second charge the retort bowl and cover are cooled, removed from the furnace and cleaned of any accumulated residue. The residue, after being ground and screened, is re-treated in the muffle furnaces at the silver refinery.

The bowls are heated in an oil-burning furnace at a temperature just sufficient to distill the selenium. Temperature control is maintained by a thermocouple indicator set in the retort cover. The retort distillate is collected in steel pans, which hold 15 lb. of selenium each. These selenium blocks are allowed to cool slowly in order to obtain the gray metallic variety. (Fig. 6.)

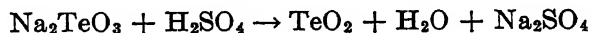
In this step, and in all others throughout the entire selenium and tellurium plants, careful control is maintained by properly prepared samples of intermediate as well as end products.

The metallic selenium blocks are held until analysis shows them to be of proper quality. Retorted selenium that contains over 0.10 per cent Te is retorted a second time. Then the blocks are broken in a small jaw crusher and ground in batches of 400 lb. each in a Patterson pebble mill. The ground selenium is screened mechanically through 150 mesh and is then ready for market. Any plus 150-mesh material is reground. Screen analysis of fine ground selenium is as follows: +200, 2.31 per cent; -200 to +300, 19.76; -300, 77.93; total, 100 per cent.

Fine selenium is packed in tins containing 5 kg., 10 lb. or 100 lb. each. The assay of fine ground selenium is 99.85 per cent Se, 0.08 per cent Te, 0.015 per cent Fe, 0.002 per cent Cu, 0.006 per cent Pb, which totals 99.953 per cent.

TELLURIUM PLANT

The precipitate formed on neutralizing, with sulphuric acid, the solution from caustic-leaching doré-furnace soda slag is the raw material for tellurium production. The principle of the neutralization is that, while sodium selenite is soluble in neutral solution tellurium dioxide is not, therefore the latter precipitates according to the equation:



Some selenium is carried down mechanically with the flocculent TeO_2 , so that this precipitate must be treated for removal of selenium before it can be used for production of tellurium. The mud is filtered through a 14-plate, 24 by 24-in. lead-plate and frame Shriver filter press. The filtrate from the neutralization is treated for recovery of selenium as described.

The TeO_2 precipitate, or "neutralized mud" as it is called assays about as follows: Cu, 2.0 per cent; Se, 6.5 per cent; Te, 32.0 per cent, with small varying amounts of silver and gold. This mud is mixed in 900-lb. batches with sulphuric acid and is charged to a reverberatory roasting furnace. There the mud is hand-rabbled for about 8 hr., during which time very nearly all of the selenium in the mud is volatilized to the doré-furnace scrubber system for recovery. In addition, the copper in the roasted mud is converted to the water-soluble sulphate. The acid

roasting is the first step in both slimes treatment and tellurium treatment. Up to this point the tellurium mud is processed in the silver refinery.

Roasted tellurium mud assays 1.8 per cent Cu, 0.25 per cent Se, 30 per cent Te. The roasted mud is ground in a small jaw crusher, screened through $\frac{1}{4}$ -in. mesh and shipped to the tellurium plant in drums containing 450 lb. each.

Leaching Tellurium Muds

To guarantee a good quality of final tellurium product, the copper is water-leached from the roasted tellurium mud. Batches charged to the lead-lined leach tanks weigh about 900 lb. The water-leached residue is filtered through a lead-plate and frame filter press. The filtrate is returned to the silver refinery for water-leaching slimes.

The water-leached residue, containing 0.15 per cent Cu, 0.35 per cent Se, 37.0 per cent Te, is hoisted from the filter-press platform back to the leach tanks, where it is boiled with 30 per cent H_2SO_4 to dissolve the tellurium. Some selenium is also dissolved from the mud but this is immediately precipitated by the addition of sodium sulphite directly to the leach in the tank.

At the completion of the leach the undissolved residue and acid leach solution are filtered through the same press used for filtering the water-leached mud.

The acid-leached residue is barreled and returned to the anode furnace for re-treatment. In this way any silver and gold that may have been in the original neutralized mud are recovered.

The acid leach solution (200 cu. ft. in volume) is pumped to a brick and rubber-lined storage tank for conditioning with common rock salt prior to sulphur dioxide precipitation of the tellurium. From this point to the final washing of tellurium precipitate, all processing equipment is rubber-lined, to withstand the hydrochloric acid in the solutions. The acid leach solution when ready for precipitation analyses about: Cu, 0.20 gram per liter; Se, trace; Te, 20.0 grams per liter; H_2SO_4 , 350 grams per liter and NaCl, 30 grams per liter. Unlike selenium, tellurium cannot be precipitated quantitatively from 30 per cent straight sulphuric acid solutions. However, the addition of 2 per cent of salt is sufficient to carry the reaction.



nearly to completion. The solution after sulphur dioxide precipitation assays less than 0.25 gram per liter Te.

Tellurium Precipitation

The equipment for sulphur dioxide precipitation of tellurium consists of two rubber-lined precipitators, 5 ft. 0 in. in diameter by 8 ft. 6 in.

high, a water-jacketed brick-lined steel gas generator 2 ft. 9 in. in diameter by 3 ft. 0 in. high and a lead-lined water-filled gas scrubber. This equipment is entirely independent of that used on selenium production, in order to guard against contamination of final products. The burner is operated at 350° F. and 8 lb. per sq. in. pressure.

After both tankfuls of acid leach solution have been completely precipitated, they are dumped to a vented rubber-lined vacuum filter box for thorough washing with water. The filtrate from this box drains through a tile pipe to the sewer. Because of the hydrochloric acid in the barren solution, it is deemed inadvisable to attempt acid recovery from this material.

After the precipitate is washed, it is dried and melted down with flour in a graphite retort. The molten tellurium is cast in bars weighing 50 lb. each and assaying as follows: 99.7 per cent Te; 0.07 per cent Se; 0.03 per cent Cu.

ACID-RECOVERY PLANT

Weak acid that is concentrated in the acid-recovery plant comes from three sources: slimes-leach liquors, tankhouse foul electrolyte after copper deposition in the purification system, and spent scrubber solutions after selenium precipitation. Sufficient storage space is provided with six 7-ft. 6½-in. diameter by 11-ft. 6-in. deep lead-lined wooden tanks to hold a complete concentrator charge of 18 per cent H_2SO_4 .

The concentrator is a Simonson-Mantius unit (Fig. 7) with a guaranteed capacity to produce in 24 hr. 20 tons of 80 per cent H_2SO_4 from 18.6 per cent acid at 125° F. The concentrator requires per ton of 80 per cent acid produced 9300 lb. of steam at 100 lb. per sq. in. and 40,000 U. S. gal. of water at 70° F. and 25 lb. pressure at floor level. The concentrator is operated only during intervals of maximum waste-heat steam production, which is during the anode and wirebar furnace melting, skimming and poling periods, from 6.00 p.m. to 7.00 a.m. daily, except Sunday.

A concentrator batch is 15 tons of 80 per cent H_2SO_4 . At the completion of concentration the batch is dumped to the outside storage tanks for cooling and settling of the sludge. The clear acid is decanted from the outside storage to the inside storage tanks, from which it is pumped by Corrosiron piston pump as required. Most of this recovered acid is used in the muffle furnaces for roasting slimes and in the neutralization of slag-leach liquors. Because of its selenium and tellurium content, no recovered acid is used in the tankhouse for electrolyte make-up, in the acid leaching of tellurium muds or in the acid boiling of gold muds in the parting plant.

Most of the sludge produced from concentrating the weak acids is accumulated in the outside storage tanks, from which it is filtered over a

vacuum filtros-block filter. The acid filtrate is recovered in a receiver and is blown by air to the inside acid-storage tanks. The concentrated acid sludge is discarded to sewer.

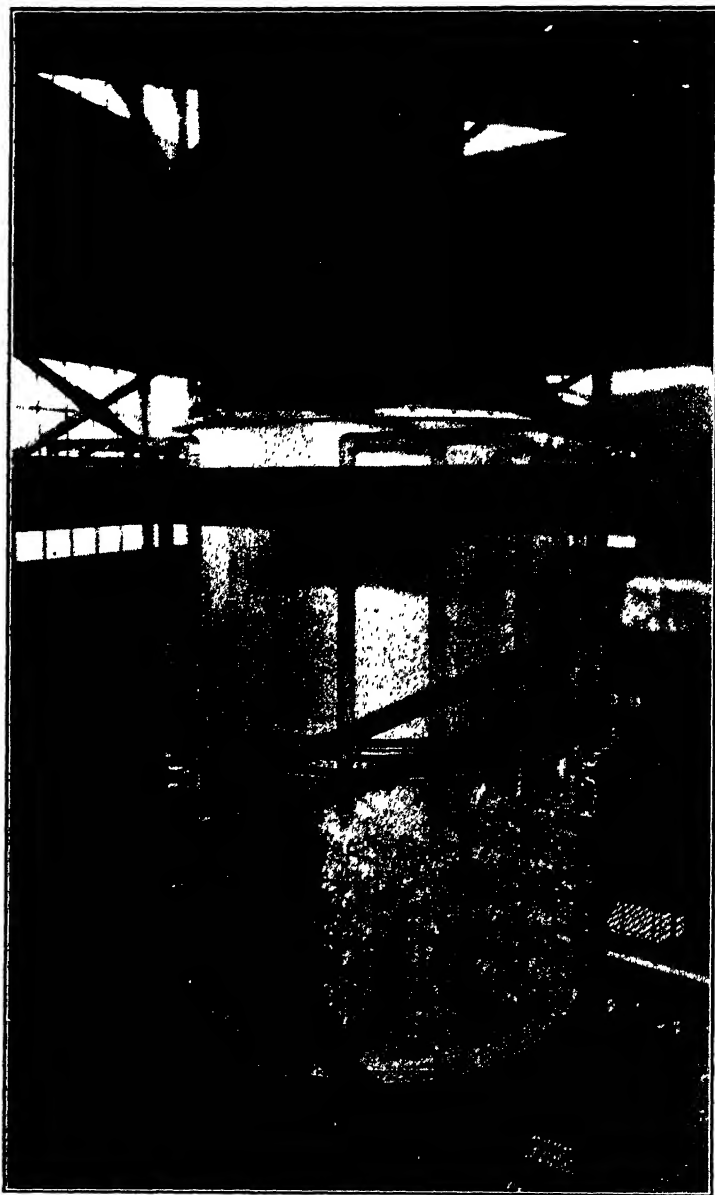


FIG. 7.—SIMONSON-MANTIUS ACID CONCENTRATOR.

Normally, between 100 and 150 tons of concentrated acid is produced per month.

DISCUSSION

(E. W. Rouse, Jr., presiding)

G. BAUMAN,* Laurel Hill, N. Y.—May I ask what the over-all recovery of selenium is—I mean, how much of the selenium present in the slime is recovered as compared with other methods used?

J. H. SCHLOEN (author's reply).—From June 1 to Nov. 30, 1937—that is the first six months of the present inventory period (we take an inventory every year)—we have lost 5.25 per cent of all the selenium we have treated. That includes all selenium lost, except about 2.5 per cent that goes back to the mine in the anode-furnace refinery slag. In other words, we have an over-all recovery of 92 per cent on the selenium coming into the plant. The summary of selenium losses for the period June 1 to Nov. 30, 1937, is given in Table 3.

TABLE 3.—Summary of Selenium Losses

Losses	Percentage of Material Treated	Percentage of Total Loss
Anode-furnace stack.....	1.23	17.2
In shapes produced.....	0.37	5.2
In cathodes shipped.....	0.10	1.4
Concentrated acid sludge discarded.....	0.24	3.4
No. 1 (Doré furnace) Cottrell..	0.24	3.4
No. 2 (selenium) Cottrell.....	0.15	2.1
Selenium solution to sewer....	2.81	39.0
Tellurium wash water to sewer.	0.12	1.7
Returned to smelter in refinery slag.....	5.26	73.4
	1.91	26.6
	7.17	100.0
Over-all selenium recovery, per cent. 92.83		

E. W. ROUSE, JR.,† New York, N. Y.—I might contribute my own part by saying that I have been able to figure pretty high selenium recoveries at times, but at the end of the month or the end of the year it was usually about 60 per cent.

D. P. WILKES,‡ Barber, N. J.—On page 524 (Mr. Benard's paper) there is the statement: "The roasted product is extracted with water leaches and the liquor pumped to the selenium

plant." I was under the impression that sodium tellurite was insoluble in water. Here is the statement: "Oxidation of the cementation slimes by roasting with caustic soda renders the tellurium soluble as sodium tellurite."

J. H. SCHLOEN.—Sodium tellurite and sodium selenite are both soluble in water solutions.

MEMBER.—In regard to recovery at Montreal East, I would like to add that this is based on the fact that there is no accumulation in the inventory in that period.

J. H. SCHLOEN.—After all, the question of metal inventories does not affect the percentage recoveries, since recoveries, as stated earlier, are based solely on amount of selenium actually treated in plant. However, metal inventories do show whether the refinery had any unaccounted-for metal loss.

H. M. SHEPARD,* Baltimore, Md.—If we do 65 per cent we consider that we are doing very well. Actually our recovery is usually slightly under 60 per cent. There have been times when we really have been scraping for selenium to meet orders and as a result a great deal of attention has been given to the recovery attained. In view of this, I am inclined to agree with the figure of 60 per cent.

E. W. ROUSE, JR.—Mr. Schloen reports that prior to some date they were throwing the selenium in the sewer.

J. H. SCHLOEN.—That's right, absolutely, 50 per cent of it. As mentioned early in our paper (pp. 495 and 496) prior to August 1934, 50 per cent of the selenium treated was recovered in the form of liberator mud and the other 50 per cent was discarded to sewer in doré-furnace soda-slag leach solutions and in scrubber solutions.

D. L. OGDEN,† Carteret, N.J.†: We at the plant have studied the question of the selenium recovery continuously. We have taken definite inventories of selenium the same as we take copper, silver and gold throughout the refinery. I think it is pretty definite that the higher the

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† Metallurgical Engineer.

‡ American Smelting & Refining Company.

* American Smelting and Refining Company

† U. S. Metals Refining Company.

grade of the selenium in the incoming material, the higher the recovery will be.

There are certain definite losses of selenium throughout the plant that are constant regardless of the amount of selenium coming into the plant, and I think that has a lot to do with the percentage recovery. In other words, the loss at Montreal would probably be constant whether they had 14 per cent selenium coming into the plant in slimes, or 22 per cent; consequently, the loss or rather the percentage loss would be much greater with the lower percentage of incoming selenium. That has been true in our case, I know.

E. W. ROUSE, JR.—When you give the statement about Cottrell, does that include the water scrubbers, or does it mean Cottrell alone?

J. H. SCHLOEN.—The recovery is for scrubber and Cottrell combined. About 85 per cent of the selenium is recovered in scrubber and the remainder in Cottrell. I did not speak of Cottrell efficiency. I spoke of Cottrell loss. What the input is, I do not know, because the flue system is peculiar for gas tests. We have run them; we have obtained 95 per cent efficiency of selenium recovery on the Cottrell from the inlet to the outlet of Cottrell, but we are suspicious of the results because, as I say, the flue system is not suitable for proper gas sampling at the inlet. At the Cottrell outlet we have extended the stacks and we are able to run proper Pitot-tube traverses, and I think the outlet figures are correct.

As regards this loss, however, we take a good deal of trouble to have a complete metal inventory every year. We even tear down the entire flue system and doré furnace. It is an expensive procedure but at least we have a certain amount of satisfaction that we are doing as well as possible in accounting for all materials that we are receiving. Yearly metal inventories are especially important to our refinery, since we handle such high-grade material. All metal losses are based on actual analyses from samples taken at point of loss.

MEMBER.—Will you explain the sampling procedure?

J. H. SCHLOEN.—On the new Cottrell, that is the selenium Cottrell, taking the gases

from only the muffle furnaces, we have two Cottrell units. The gas volume from one of these is only about 900 cu. ft. per minute, so we have combined the two stacks in order to obtain satisfactory Pitot-tube readings.

The distance from Cottrell units to gas-sampling point in the 15-in. diameter stack is about 12 ft. or so. We have taken the Pitot-tube traverses about 3 ft. from the top of the stack. Here we have fairly uniform motion of gas and we have determined a point of average velocity in the stack, at which point our sampling tube is inserted. This procedure does not differ from that recommended by the Western Precipitation Company.

We use a glass sampling tube. From the tube the gas is drawn through a series of four glass funnels and condensate bottles. Each funnel supports a perforated porcelain disk inside it. On the disk are packed a 2-in. thickness of glass wool, a $\frac{1}{8}$ -in. bed of asbestos fiber and a second 2-in. thickness of glass wool. As soon as the third filter shows any trace of color, a fresh filter is placed at tail end of the train and the first filter is removed. As necessary, condensate bottles are replaced. The gas from the fourth filter is passed to a drip bottle and then to a Sprague gas meter, and so to the exhaust jet.

Hourly readings are taken of meter volume, meter pressure, meter temperature, stack temperature and stack-gas velocity. Collections are changed weekly. We have tried bubbling the gas from the last filter through stannous chloride which, as far as I can find out, is about the best reducer to detect any traces of selenium dioxide. In every case the stannous chloride showed negative results, so we feel quite sure that the selenium loss as reported at the new Cottrell is as shown. Much the same procedure is used to determine selenium and other metal losses from the doré-furnace Cottrell stacks. The losses from the doré-furnace Cottrell are somewhat higher than those from the selenium Cottrell, but, as far as these losses go, they are small. Our main loss is in selenium solution to sewer. Say we lose 5 per cent of all the selenium being treated around the plant and then besides that the 2.5 per cent of selenium going back to the smelter, for which we are not paid. How much of this selenium the smelter loses we do not know. But the main loss of selenium around the plant

is in the discarded solution. Of the 5 per cent we lose, 55 per cent is in selenium solutions to sewer, or about 3 per cent of all the selenium we treat. Actually, from our gas tests we show a loss from Cottrell stacks of only 0.4 of 1 per cent of all the selenium treated in plant, so, if our gas-testing method is accurate to, say, 50 per cent, we feel quite content, and I am sure it is much more accurate than 50 per cent. The accuracy of the method is probably plus or minus 10 per cent.

C. H. ALDRICH,* Carteret, N. J.—We have made a great many tests trying to find just where the losses of selenium occur. It is quite easy to determine losses that occur in solution, going to sewer and residue, and things that can be collected and then accurately sampled, but we have never been entirely satisfied with the results on our gases going from the Cottrell.

We have used methods like those described by Mr. Schloen, but we have always had the feeling that something was getting away which was not recovered by the ordinary methods of filtration and separation of fumes such as he has described.

We do not know exactly what it is, but we have had a feeling that there was some sort of fixed gas in the selenium which was escaping, because that seemed to be the only place that we could not determine and prove with any degree of certainty. I hoped Mr. Schloen was going to have something more definite on that phase of it.

D. L. OGDEN.—I might enlarge a little on Mr. Aldrich's statement. We used practically the same method that Mr. Schloen described. We were using an American Meter Company's dry meter, and had to dry the gas before sending it through the meter. We found that we obtained more selenium in the sulphuric acid than we did in the filter medium. This led us to believe that there was some gas, hydrogen selenide, or something of that sort, that was going through the entire system and being picked up by the sulphuric acid. We had no way of determining it, since if we put two bottles of sulphuric acid in the train, we would get selenium in both bottles, so it has always been our opinion that the losses on

the Cottrell were rather large, and we were never definitely able to pin them down. We know that there is a certain vapor tension of selenium dioxide in air and that this is increased by the quantity of water vapor in the air. Mr. Bauman at that time was working at the plant and did considerable work on it, in connection with volatilizing selenium dioxide and actually determining the vapor tension in the gas after collecting whatever selenium dioxide could be collected, but in spite of that we feel that there is some gas carrying selenium that is not collectible by the ordinary methods.

E. W. ROUSE, Jr.—I wonder whether there is any question of very high recoveries at one place and relatively lower recoveries at some place else. There may be a question of assays of the incoming materials.

J. H. SCHLOEN.—All incoming material, every piece of material we receive, that contains selenium, either blister or anodes, is sampled 100 per cent. We do not use percentage sampling. On blister we use a half template; on anodes, a quarter template. We have our splitting limits on selenium assays. Our assays agree within the splitting limits. What more can anyone want?

E. W. ROUSE, JR.—As a shipper I would be very happy to have a 95 per cent recovery. It might depend on whether you are buying or selling.

J. H. SCHLOEN.—You can look over the figures, but I believe that the reason for our high recovery is definitely the type of scrubber employed, plus the fact that we eliminate the large portion of our selenium during the first step in our flowsheet. We have tried the rain plates on scrubber and there was a lot of trouble. We had losses, yes, when we started up; we did not have a well equipped scrubber and we did not have any Cottrell. It took very nearly two years to solve the problem until the Cottrell was built. Now, regardless of whether our losses on the attacks are 50 per cent, or even 75 per cent out (and we do agree on the material assays as it is shipped in), we account for everything every year. I do not see where the argument lies.

* U. S. Metals Refining Company.

E. W. ROUSE, JR.—I would like to ask a further question. The waste selenium is selenate selenium?

J. H. SCHLOEN.—Yes.

E. W. ROUSE, JR.—Are any special means taken to be sure that the selenium in your later slags is selenite and not selenate?

J. H. SCHLOEN.—No.

E. W. ROUSE, JR.—They just happen to be good.

J. H. SCHLOEN.—No, not that. We do not use niter until we have practically all the

selenium out of our matte in the doré furnace. You could possibly remove all selenium from matte by using soda and air but you cannot do it within a reasonable time. By adding niter you get a much faster reaction, but you get some selenate selenium which is not reduced by SO_2 in sulphuric acid solution later on. Blowing with soda does not produce sodium selenate. If you precipitate selenium from a hydrochloric acid solution, you can recover selenate selenium. But since we precipitate, using a straight sulphuric acid solution, we keep the niter out of doré furnace as long as we can.

Recovery of Selenium and Tellurium at Copper Cliff, Ontario

BY FREDERIC BENARD,* MEMBER A.I.M.E.

(New York Meeting, February 1938)

RECOVERY of selenium and tellurium at Copper Cliff by the Ontario Refining Co. has been previously described by the writer.¹ During 1935 a new building was erected to house this operation and description of the new plant and process form the subject of this paper.

The building, of modern steel and tile construction, covers an area of 5900 sq. ft. with a volume of approximately 165,000 cu. ft. The large monitored center bay is flanked by two smaller outside bays, one of which is devoted to the tellurium section. All equipment, ceilings and upper walls, are treated with aluminum paint, giving good illumination and facilitating good housekeeping, essential from a health standpoint in handling material of this nature.

EQUIPMENT

Layout and type of equipment conforms to the requirements of the process as described below. In the selenium section, storage tanks, neutralizing tanks and precipitators are of steel construction, lead-lined and arranged for gravity flow (Fig. 1). The neutralizing tanks are equipped with water-cooled lead coils for controlling solution temperature, agitation being accomplished with compressed air. The precipitators are provided with mechanical agitators, and sulphur dioxide is introduced into the solution through 1/2-in. lead pipes leading from a manifold attached to the cover of the precipitator. Each precipitator has internal cooling coils and an air-jet exhaustor to carry off fumes. Neutralized solutions are filtered in a 29-plate wooden filter press using heavy cotton duck as a filter medium, forced feed being maintained by a Welmet centrifugal pump. Dilute solutions are concentrated by evaporation in a vacuum evaporator, constructed of cast hard lead. Heat is supplied by an outside steam chest operating under 15 lb. steam pressure. The solution is circulated through the steam chest by a pump of antimonial lead at a rate approximating 400 cu. ft. per min. The evaporator is evacuated by a water-jet condenser that creates a vacuum of 26 in. of mercury under normal operating conditions. The capacity of the vessel is 60 cu. ft. and the rate of evaporation 25 cu. ft. per hour.

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* Plant Manager, Ontario Refining Co., Ltd., Copper Cliff, Ont.

¹ *Trans. A.I.M.E.* (1933) 106, 391.

The grinding room (Fig. 2) is equipped with a 16-in. rod mill, 5 ft. long, charged with casehardened steel rods. The mill is fed by a mechanical screw feeder and discharges into a 27-in. supported centrifuge provided for the purpose of washing and dewatering. Final drying is carried out in two steam-heated drying cabinets at 180° to 190° F.

In the screening room, two motor-driven Rotex screens are used for screening the final product through 200-mesh phosphor-bronze wire cloth. Each screen is equipped with a variable-speed mechanical feeder and handles approximately 50 lb. per hour. Steel boxes are provided for storing the final product.



FIG. 1.—SELENIUM SECTION.

Equipment used in the recovery of tellurium (Fig. 3) includes four rectangular V-bottomed steel tanks for leaching and purifying. Filtration is effected by a four-leaf suction filter acting under 20 in. of vacuum supplied by a Hytor vacuum pump. In addition, two suction-box filters are provided for handling precipitated oxide. Drying is accomplished in an insulated, steel drying cabinet heated with low-pressure steam.

In the reduction of oxide to metallic tellurium an oil-fired tilting crucible furnace is used, fumes being thoroughly taken care of by an exhaust fan of ample capacity. Pulverizing and mechanical screening equipment sizes the product to market requirements.

PLANT FEED

All feed to the combined sections is received in the form of solutions derived from treatment of the various by-products of silver-refinery

processes in which selenium and tellurium are concentrated (Fig. 4). The principal sources of these solutions are described briefly as follows:

Niter Slag.—The selenium content of slimes and sludges composing a doré charge is partly recovered in niter slag during the refining period. Water-leaching of this material yields a basic solution containing selenium and tellurium as selenites and tellurites.



FIG. 2.—GRINDING ROOM.

Selenium Whiskers.—Each furnace operation unavoidably volatilizes an appreciable quantity of selenium. Part of this is oxidized to selenium dioxide which, on cooling, crystallizes in chambers provided in the flue system for this purpose. A mat of needlelike crystals is formed, containing roughly 55 per cent selenium, which is readily soluble in water, forming selenious acid.

Scrubber and Cottrell Solutions.—The silver-refinery flue gases are treated in a water-spray scrubber and a wet Cottrell for the recovery of

valuable constituents. Soluble selenium and tellurium entering this system are recovered in solutions, which are filter-pressed and pumped directly to the selenium plant. Assays of Cottrell solutions average 33.8 grams per liter Se and 2.4 grams per liter Te, and scrubber solution 21.8 grams per liter Se, and 1.0 grams per liter Te.

Cementation Slimes.—Leach liquors from the slimes-leaching treatment are freed of selenium and tellurium by cementation with copper sludge. This process concentrates tellurium in the cementation slimes, which, from time to time, may be profitably submitted to special treat-



FIG. 3.—EQUIPMENT FOR RECOVERY OF TELLURIUM.

ment for quick extraction of tellurium. Oxidation of the cementation slimes by roasting with caustic soda renders the tellurium soluble as sodium tellurite. The roasted product is extracted with water leaches and the liquor pumped to the selenium plant.

SELENIUM PROCESS

The selenium process consists of removing base metals and tellurium from the feed solutions by neutralizing and filter-pressing the neutral solution. The resultant press sludge comprises the feed to the tellurium plant, while the effluent liquor is charged in batches to precipitators. After being made up to 12 per cent H_2SO_4 by volume, it is gassed with sulphur dioxide to precipitate selenium. The granular product is water-washed free of acid, pulverized in a rod mill, dried, screened through 200 mesh and blended to market specifications.

Incoming feed solutions from the silver refinery are received in the storage tanks and held until sufficient quantity is on hand to make up a batch. At the start of a batch, solutions from the storage tanks are run into one of the neutralizing tanks, acid and basic solutions being blended in this operation to approximate neutrality. The solution is then sam-

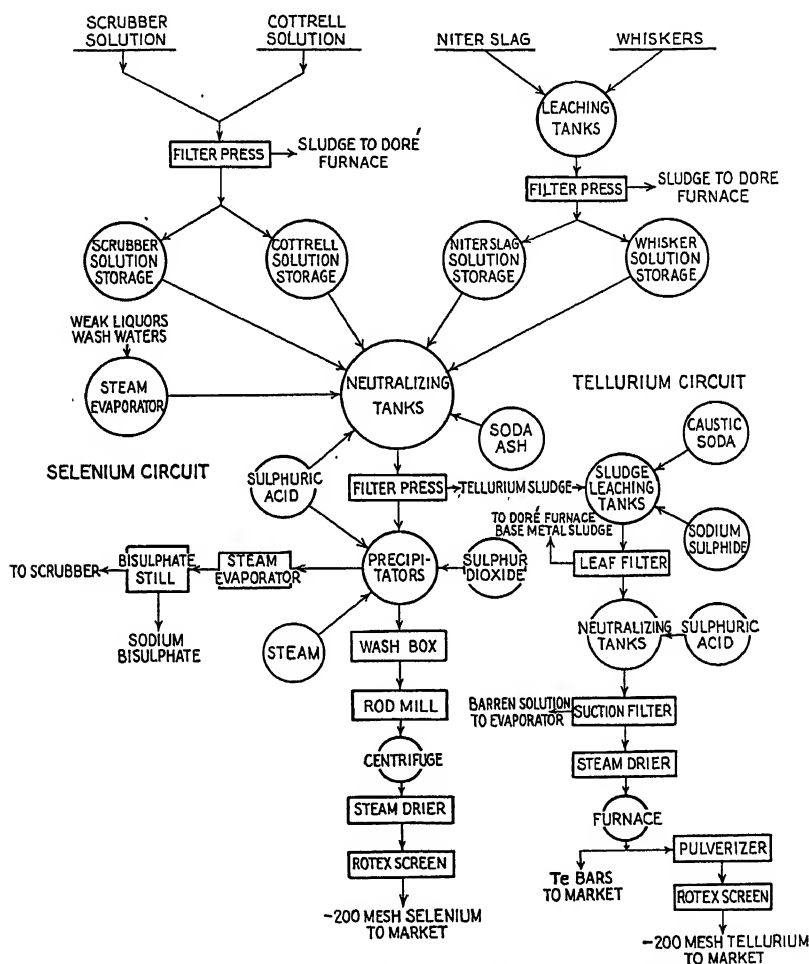


FIG. 4.—FLOWSHEET OF SELENIUM AND TELLURIUM PLANTS.

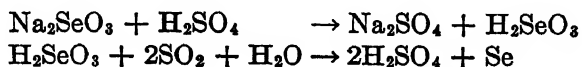
pled and a rough determination of the selenium content is made. The desired concentration of selenium is 120 to 140 grams per liter, since any tellurium and base metals not completely removed by neutralization will appear in reduced percentages in the final product if the selenium content of each batch is high. Solutions containing less than 120 grams per liter Se are filter-pressed and concentrated in the evaporator to the required strength and then returned to the neutralizing tank.

Since the purity of the final product depends principally on the removal of impurities by neutralization, this operation is carried out with care. The solution is first made distinctly acid to litmus by adding sulphuric acid, and then brought back to the neutral point by mixing in soda ash solution until the batch solution shows no effect on red and blue litmus. This ensures precipitation of the base metals, particularly lead and copper as carbonates.

After thorough agitation, a sample of the solution is filtered and divided into two portions. One drop of dilute sulphuric acid is added to one portion and one drop of dilute soda solution to the other portion. If both solutions remain clear, this test indicates that tellurium has been removed as far as possible and the neutralization is considered complete. This control test is necessitated by the fact that tellurium is soluble on either side of the neutral point and is regarded as conclusive. Other methods of testing, based on hydrogen-ion reaction with colorimetric indicators, have been tried but failed because of oxidation of the indicator dyes by selenious acid.

The neutralized solution is filter-pressed into a storage tank, from which it is charged to the precipitators in 60-cu. ft. batches. A typical analysis of the solution after filter-pressing is 125 grams per liter Se and 0.75 grams per liter Te. The filter-press cake, containing the base-metal impurities and tellurium, is water-washed and sent to the tellurium plant.

In the precipitators, selenious acid and sodium selenite are reduced to metallic selenium by the action of sulphur dioxide gas in acid solution, according to the following reactions:



Selenium present in the higher state of oxidation as selenic acid or sodium selenate is not precipitated by sulphur dioxide in sulphuric acid but may be reduced in hydrochloric acid solutions. The small quantity of selenate present in the solutions treated does not warrant the installation of the necessary equipment for handling strong hydrochloric acid.

The batch in the precipitator is made up to 12 per cent H_2SO_4 by running in the required amount of commercial acid. The heat generated by the reaction is carried away by circulating water through the cooling coils. When the temperature of the solution has been reduced to 90° F., slow gassing is started and maintained for about six hours. At this stage the solution appears bright red, because of the precipitation of amorphous selenium. The gas flow is then increased and the solution heated to 180° F. by introduction of live steam.* After approximately 20-hr.

* Canadian Patent No. 303480.

treatment under these conditions the amorphous precipitate has been converted by the heat to gray crystalline selenium, which settles to the bottom of the precipitator. The reaction is considered complete when a filtered sample shows only a faint pink shade on heating and gassing with sulphur dioxide.

Precipitation of selenium is not complete at this point, 5 to 7 grams per liter Se remaining in solution, but additional gassing tends to precipitate tellurium. A typical assay of the spent solution shows 5 grams per liter Se, 0.4 grams per liter Te, and 380 grams per liter H_2SO_4 . Fig. 5 shows the rate of precipitation of the selenium during the gassing cycle.

The contents of the precipitator are agitated for 2 to 3 hr. after completion of the gassing, then allowed to settle. The spent solution is siphoned off and the precipitated selenium washed with one 5 per cent acid wash followed by three hot-water washes. The spent solution is pumped to the silver refinery, evaporated to 50° Bé and charged to a cast-iron still, where the selenium and acid are driven off and recovered in the scrubber and Cottrell system. The molten residual sodium bisulphate is cast into slabs and sent to the smelter. Wash waters are used in the slimes-leaching process in the silver refinery.

The washed selenium is dumped from the precipitator into a suction filter box, where washing is continued with hot, filtered steam condensate until the effluent wash water tests free of acid. A few pounds of soda ash is then mixed with the selenium to ensure neutralization of any occluded acid freed by grinding and the mixture is charged to the rod mill at a rate of 150 lb. per hour. Fines are washed out of the mill by a stream of water into the centrifuge, where the ground product is water-washed until free of soda ash. After this final washing the selenium is shoveled into enamelware pans and dried in the drying cabinets for 24 hours.

The dried selenium, which now appears as a black amorphous powder, is screened through 200 mesh and the oversize is returned to the mill. Undersize material is carefully sampled and stored in steel boxes until the assay is received. A typical assay of the finished product is: Se, 99.70 per cent; Te, 0.12; ash, 0.13; Cu, 0.001; Fe, 0.01.

Selenium is shipped to the market in 8-gal. kegs holding 100 lb., and 20-gal. kegs holding 300 lb. A small quantity is supplied to consumers in 10-lb. tins.

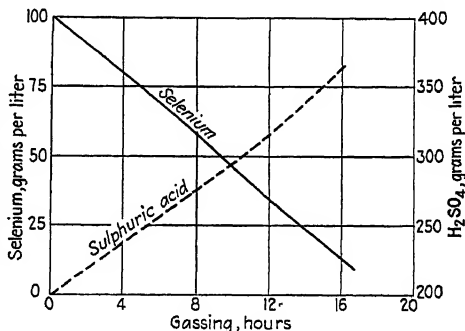


FIG. 5.—RATE OF PRECIPITATION OF SELENIUM DURING GASSING CYCLE.

TELLURIUM PROCESS

The crude tellurium sludge from the selenium process is charged in lots of 2000 lb. to a dissolving tank. About 100 cu. ft. of cold water is added and the mixture agitated with an air jet to ensure suspension. Flake caustic soda is added in small increments with continuous agitation, until the color of the suspended solids changes from gray to dark brown. This darkening of the mixture is caused by the dissolving of the light colored tellurium oxide, which leaves dark base-metal hydroxides in suspension.

The sludge of base-metal hydroxides is filtered out of the liquor on the leaf filter and the clear filtrate, containing tellurium as sodium tellurite, is discharged into a neutralizing tank. The base-metal sludge is returned to a dissolving tank where it is again leached with strong caustic to remove any tellurium residue. The sludge is again filtered out and returned to the silver refinery doré furnace. The filtrate from this second leach is used in the make-up of subsequent batches.

In the neutralizing tank, the filtered caustic liquor is neutralized by addition of dilute sulphuric acid. This operation precipitates tellurium oxide, leaving selenium in solution. Lead sulphate and some silica are also precipitated. After settling, the barren solution is decanted and sent to the selenium plant, where it is evaporated and the selenium recovered. The precipitated oxide is given four water washes by decantation and then redissolved in caustic solution.

In redissolving the oxide, care is taken to avoid a large excess of caustic soda. This precaution leaves the silica undissolved, tellurium and lead entering the solution. Sodium sulphide solution is cautiously added, to avoid excess, and precipitates lead as lead sulphide. Any excess of sulphide in solution precipitates a mixture of tellurium and sulphur.

The lead-free caustic solution is filtered through a suction box into the second neutralizing tank, where it is heated to 180° F. and again neutralized with dilute sulphuric acid. This precipitates substantially pure oxide, which is thoroughly water-washed by decantation, dewatered in a suction box and placed in enamelware pans in the drying cabinet. The dry oxide is rolled to a powder, mixed and sampled. A typical assay of this product is: Te, 77 per cent; Se, 0.03; Pb, nil; SiO₂, 0.02.

Tellurium oxide is reduced to the metal by mixing with flour and borax and heating in a covered crucible in the tilting furnace. The usual charge consists of 110 lb. of tellurium oxide, 24 lb. of grain flour, and 13 lb. of borax. The oxide, flour and 10 lb. of borax are thoroughly mixed by rolling and then charged to the crucible. The additional 3 lb. of borax is spread over the top of the charge as a cover.

As heating of the charge progresses, reduction of the metal begins at a comparatively low temperature and is complete at a dull red heat. Dur-

ing the reduction, white fumes of oxide are continually given off. When reduction is complete, the molten bath of metal is entirely covered by the borax slag and the fuming ceases. When this point is reached, the melt is cast into an iron mold. In casting the melt, some slag is first poured into the mold, to protect the latter from the action of the hot metallic tellurium, which readily combines with iron. During casting, dense fumes are evolved, necessitating the use of a gas mask by the operator.

When cool, the bar is dumped out of the mold and adhering slag is chipped off. The metal is sampled by making four saw cuts in the bar. Each melt yields about 80 lb. of metal, which assays as follows: Te, 99.75 per cent; Se, 0.04; Pb, trace.

Tellurium is shipped to the market as bars, lump metal and pulverized metal. Bars and lump metal are shipped in boxes. When pulverized tellurium is required, the metal is ground in the Mikro pulverizer, screened to specifications, and shipped in kegs holding 200 pounds.

ACKNOWLEDGMENT

The writer wishes to express his thanks for assistance rendered in the preparation of this paper by R. H. Waddington, assistant plant manager, and H. A. MacDougall, in charge of technical control, Ontario Refining Co., Copper Cliff, Ontario.

DISCUSSION

(See page 517.)

Recent Progress in Tin Smelting and Metallurgy

By C. L. MANTELL,* MEMBER A.I.M.E.

(Cleveland Meeting, October 1944)

WHEN considered from the viewpoint of world annual output, tin is one of the rarest metals. Its annual production is exceeded by that of iron, copper, lead, zinc, aluminum, magnesium; probably by that of the ferroalloys of manganese, chromium, and silicon, and possibly by the world production of sodium; while it exceeds only the output of such common metals as nickel, antimony, mercury, tungsten, molybdenum, silver, gold and the precious metals.

Cassiterite, or tinstone, until the second World War was the only mineral that was an important source of tin. This mineral is frequently called "tin ore." The use of the term should be restricted to the ore containing the mineral, and not, in addition, to the concentrates of the mineral obtained from the ore or from stanniferous alluvial deposits. There is a general misuse of the term "tin ore" in the Malay Peninsula and adjacent localities, particularly where most of the mineral is obtained from secondary stanniferous deposits. The term "cassiterite" is exclusively used in mineralogical, geological, and other scientific writings; it is unfortunate that it is not more frequently used when referring to the occurrence of the mineral on an economic scale.

ORES

"Tinstone" is a very convenient old English term deserving a more frequent use. Tinstone is a dioxide of tin, or stannic oxide. When chemically pure, as in the very

rare transparent variety, it has a metallic content of 78.6 per cent tin. Frequently, however, the crystals and grains contain appreciable amounts of impurities, chiefly iron and tantalum. The impurities here referred to are those actually in the mineral itself.

Tinstone usually has a deep brown or black color with an adamantine luster. Several other colored varieties are known, among them red ruby tin, yellow rosin tin, and yellow wax tin, the names in each case being descriptive of the mineral's appearance.

Ainalite is a variety of cassiterite containing almost 9 per cent of tantalum pentoxide. Sparable tin, tooth tin, and needle tin, as a result of their acute ditetragonal pyramidal crystalline form, receive their names from their crystallographic appearance. Wood tin is a compact variety of cassiterite composed of radiating fibers resembling dry wood. Toad's-eye tin is a similar variety on a smaller scale in which the fibers appear to resemble the eye of a toad. Stream tin is water-worn tinstone. Float tin is sometimes employed to describe the cassiterite occurring in soil derived from the weathered surface of a mineralized area.

Stannite is an ore of tin of lesser importance than cassiterite. It is a sulphide of tin, copper, and iron, sometimes known as tin pyrites or bell-metal ore. Its chemical composition is sometimes expressed by the formula $\text{Cu}_2\text{S.FeS.SnS}_2$ with zinc usually present in varying quantities. The tin content varies from 22 to 27 per cent and there is about 29 per cent of copper, 13 per cent of iron, and 30 per cent of sulphur.

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* Consulting Engineer, New York, N. Y.

The color of the mineral stannite is steel gray when pure, but the usual variety is frequently iron black, sometimes bronze or bell-metal color, and occasionally has a bluish tarnish. The presence of an admixture of copper pyrites causes the mineral to assume a yellowish color.

Stannite has a metallic luster and gives a blackish streak. Its specific gravity is 4.3 to 4.5—considerably less than cassiterite—with a hardness of 4 on the Von Mohs scale. When heated in an open tube it gives off sulphur. When treated by the blowpipe on charcoal, it fuses eventually to form a brittle, metallic globule. The reactions for iron and copper are given by the roasted mineral with borax.

Only in Bolivia has stannite been proved to occur in quantities of economic importance.

Cylindrite has been discovered in recent years in Bolivia in sufficient amount to justify special ore-dressing methods for milling it. It owes its name to the cylindrical shell-like fragments into which it cleaves. It is a complex lead-tin-antimony sulphide, its composition being represented by the formula $Pb_8Sb_2Sn_8S_{11}$. Its color is blackish lead gray, its luster metallic, its streak black. Its specific gravity is much lower than that of cassiterite but higher than that of stannite, being 5.42, but it is much softer than either of the other minerals, being 2.5 to 3 on the Von Mohs scale. It is often associated with stannite and cassiterite in veins along with franckeite, sphalerite, pyrite, proustite, and quartz. A typical high-grade specimen of cylindrite is a compact lead-gray mixture of sulphides, which are quite soft and dirty the hands. The cylindrical shells of cylindrite are prominent on the broken surface of the ore.

Another complex sulphide of tin is franckeite, which is very similar to cylindrite except that it has perfect cleavage in one direction. It is a blackish gray to black mineral with a metallic luster, generally associated with cylindrite. Its com-

position is represented by the formula $Pb_8Sb_2Sn_8S_{11}$, containing therefore a smaller percentage of tin than cylindrite. Its specific gravity is slightly higher than that of cylindrite, being 5.5, and its hardness is approximately the same as that of the latter mineral, being 2.75 on the Von Mohs scale. Franckeite often occurs massive with imperfect radiated and foliated structure. It is found in certain veins in Bolivia associated with the same minerals ordinarily found with cylindrite.

With the opening of American smelters, disruption of trade routes and realignment of ore sources, loss by the Allies of the major portion of the world's supplies of alluvial ores in the Malay States and the Dutch East Indies, there has arisen a situation of dependence on Bolivian and Mexican ores for the tin supply of the United States. As a result, stannite, cylindrite, franckeite and complex tin ores have become economically important. Ore-dressing processes have been developed for them. As ore sources they greatly complicate tin smelting. Their consideration is important as a background of understanding the reasons for the far greater complexity of the American Longhorn tin smelter and the necessity of chemical processing therein as compared with the relatively simple processing in the smelter of Straits Trading Co. and the English plants.

TIN DEPOSITS

Tin as an element forms less than 0.001 per cent¹ of the igneous rocks in the earth's crust. Only a small fraction of the earth's granite masses is stanniferous. It is thought that there are no exceptions to the rule that primary tin deposits occur in or near an acid igneous rock such as granite, or related rocks like granite-porphry, quartz-porphry, aplite, pegmatite, or quartz. These rocks generally occur as veins traversing granite and metamorphosed rocks of sedimentary origin, as illustrated by schists,

¹ References are at the end of the paper.

phyllites, slates, and quartzites, and metamorphosed limestone in some tin fields.

While it is true that tin fields occur in connection with acid igneous rocks, the converse is not true, for there are extensive areas of granitic rocks that contain no tin minerals. In Pahang, in the Federated Malay States, the Benom and the Main Range of the Peninsula run approximately parallel, only about 12 miles apart. Tin is mined extensively in the Main Range, while the Benom Range has failed to show the existence of any tin deposits in it. Mica, muscovite, and lepidolite are abundant in the Main Range but absent in the Benom chain; while hornblende, widely distributed in the Benom granite, is rare in the Main Range.

Stanniferous veins are generally more common on the margins of granite masses, where the fissuring is more pronounced. The greater portion of the world's supply of tin minerals is obtained from granite contact lodes.

Chronologically, in respect to their discovery and working on a considerable commercial scale, the tin fields of the world are those of (1) the west of England, Brittany, and the Erzgebirge; (2) Burma, Siam, the Malay States, and the Dutch East Indies; (3) Bolivia; (4) Nigeria; (5) Australasia; and (6) Mexico.

SMELTING

Tin concentrates are the product of open-cut mining, hydraulic sluicing, gravel-pump operation, or dredging when applied to alluvial deposits, or by lode mining in conventional fashion.

Ore-dressing methods are relatively simple when pure oxide ores are handled, but increase in complexity as the ore complexity increases. Flowsheets of most of the important mines are available in the mining literature.

It is often necessary to treat specially the tin concentrates⁸ from some localities

so as to remove objectionable metallic impurities, with the object of making them more suitable for smelting and the production of a purer final metal. Concentrates from vein deposits such as Bolivian may require extensive preparation before smelting. Concentrates from alluvial sources require relatively little pre-treatment.

Although the literature on tin ores, smelting and metal purification is not abundant, because of a small number of plants, technical references are available. H. Louis^{2,3} described ore reactions and smelting in shaft and reverberatory furnaces, W. R. Jones⁴ extensively described ores and the tin mines of the world from the geologic and mining viewpoint, R. L. Hallett⁵ reviewed world practices in the metallurgy of tin, Mantell,⁶ as a result of intensive experimental work and collection of data from original sources, augmented the technical literature. Mantell and Lidle⁷ further increased the available information in reference to secondary smelting and tin recovery from nonmineral sources, Fink and Mantell^{8,9} described their studies of gaseous reduction, leaching, smelting, metallic reduction, treatment of Bolivian concentrates, and electrolytic refining in their relation to winning of tin from impure Bolivian vein ores.

There are a number of general methods,⁸ which may be broadly classified into: (1) roasting followed by further mechanical separation of minerals that have been physically broken away from the cassiterite as the result of the process or altered in such a manner, e.g., as change in specific gravity, making them more amenable to further mechanical concentration; (2) roasting under controlled conditions followed by leaching with water or acid solutions; (3) heating with sodium salts such as soda ash, sodium chloride, salt cake, etc., followed by leaching; (4) metallic impurity removal by oil flotation when the impurities are present as sulphides. These will be discussed rather briefly.

When calcined⁵ at a red heat, cassiterite is unchanged but many of the associated minerals of metals other than tin are altered. Much of the sulphur and arsenic and some of the antimony are volatilized. The volatile products, particularly arsenious oxide, are sometimes collected, either in baghouses, Cottrell installations, or other dust-collecting equipment. The roasted concentrates contain tin oxide, oxides of iron, zinc, bismuth and copper, lead sulphate, small quantities of more or less unaltered sulphides, tungsten compounds, and minor amounts of other minerals.

Roasting is done in furnaces of many types, either of a hand-rabbed reverberatory variety or in multihearth mechanical furnaces.

Roasting is often followed by leaching with water or acid solutions, to remove the products made soluble by the roasting process.

Tungsten-bearing tin concentrates are usually heated with sodium carbonate or sodium sulphate at 600°C., to form sodium tungstate. Excess sodium salt is avoided, otherwise some of the cassiterite will be converted to sodium stannate. The sodium tungstate is soluble in water and is leached from the treated concentrates, recovered from the leached liquors by evaporation, and purified for the market.

When the concentrates carry considerable quantities of sulphides, a chloridizing roast, followed by leaching, is sometimes used. This method⁶ is often employed on Bolivian silver-tin ores and silver-tin-lead concentrates. When the sulphides are roasted with salt (NaCl) in an oxidizing atmosphere, sodium sulphate and the chlorides of the metals are formed with no attack on the tin oxide. Many of the chlorides are fairly volatile. Bismuth, lead, arsenic, antimony, and silver may be thus partially removed in the form of fume. The chloridizing roast is usually followed by suitable leaching and washing in wooden

vats, sometimes fitted with filter bottoms. The furnaces for the chloridizing roast are similar to those used for dead roasting except that 1 to 5 per cent of salt (NaCl) is mixed with the concentrates before they are charged into the furnace.

METALLURGY

Practically⁵ the only source of primary tin is the stannic oxide ore, cassiterite. The winning of tin from its ores consists essentially of causing the conversion of the stannic oxide, SnO_2 , to elemental tin. This can be accomplished in a variety of ways, only one of which is now in commercial use and of present economic importance.

Stannic oxide can be reduced by carbon at fairly high temperatures. Cassiterite can be reduced to tin metal by certain reducing gases, such as hydrogen and carbon monoxide; commercial gases containing these or mixtures of them; or at a lessened rate by hydrocarbons and gasified oils.

The possible metallurgy of tin divides itself naturally into several subdivisions by following through the analogy of other non-ferrous metals:

1. Reduction and removal of oxygen by carbon and related solid reducing agents.
2. Reduction and removal of oxygen by gaseous reducing agents.
3. Leaching of the ore (as in the case of copper) with direct separation of the metal from the leaching liquors.
4. Converting stannic oxide to a soluble form and decomposing the compounds formed.
5. Solution and decomposition in a fused salt bath (as the Hall process for aluminum).
6. Electrolytic reduction at the cathode in aqueous solutions.
7. Reduction of cassiterite by metals.
8. Combinations of these methods or combinations of parts of them, such as leaching with acids in advance of roasting or smelting, or preliminary roasting fol-

lowed by leaching followed by carbon smelting.

The only commercial method today is the first in the classification, that of reduction by solid carbonaceous material. The second, that of gaseous reduction, is, because of its manifold advantages, a method of the future. In the newest tin smelter, acid treatment or leaching of the ore for the removal in a selective manner of some of the impurities prior to smelting is followed.

The reduction of tin from its oxide is not difficult. Reduction takes place readily at fairly high temperatures in the presence of reducing agents such as coal, culm, or coke. The required temperature for smelting is determined principally by the composition of the slags that are formed. The smelting temperature must be sufficiently high to keep the slags fluid, and allow the reduced tin metal to settle and collect in the bottom of the furnace.

Inasmuch as the smelter has only one ore to deal with, the metallurgy of tin is comparatively simple. Its reduction in practice is almost invariably accomplished by the aid of carbonaceous materials. Several complications occur, however:

1. The temperature of reduction is so high that the oxides of other metals, present in a greater or lesser degree, are reduced at the same time. These metals may produce undesirable and troublesome tin alloys. The iron-tin alloy, "hardhead," is an example.

2. Tin oxide is amphoteric. Unless conditions are carefully regulated, the furnace linings are attacked.⁵ Siliceous acid linings cause tin silicates to be formed; basic linings of lime or magnesia result in losses as stannates. The great difficulty in tin smelting is caused by the fact that tin oxide readily combines with silica to form tin silicates. During the smelting of the concentrates mixed with flux and fuel, a considerable amount of tin invariably combines with silica and goes into the slag in the form of readily fusible tin silicates

mixed with other more or less complex silicates that make up the slag. On the other hand, if an extremely basic slag is used, tin oxide will act as an acid and enter the slag. The slag components must be nicely adjusted. It is desired to produce slags of as low a tin content as possible, as the principal loss in tin smelting is in the tin carried off by the slags. The making of low-tin slags, however, is not of the greatest importance in the primary smelting of tin concentrates.

3. Tin metal at elevated temperatures is more fluid than is mercury at ordinary temperatures. It finds the most minute openings for escape and soaks into the porous refractories of furnaces to an amazing degree.

4. The slags produced contain appreciable quantities of tin. This metal must be recovered. Slags require further treatment also; there may even be treatment of successive slags for their tin content. Part of the tin in the slags is present mechanically retained as "prills," or small metallic globules. Unduly large amounts of metal go into the slag, which may run 10 to 25 per cent tin.

STAGES IN SMELTING

There are, therefore, three stages in the smelting of tin ores or concentrates⁶: (1) reduction, or tin smelting proper; (2) cleaning the slags and furnace linings and recovery of tin from them; (3) refining the impure tin.

Inasmuch as in general they represent three different practices as a function of locality, fuels, types of ores, and increasing difficulty of treatment, descriptions will be given of six smelters. The first is that of the Straits Trading Co. at the Pulo Brani Works at Singapore, Straits Settlement, Federated Malay States, where the ores are relatively pure as a function of their alluvial origin. The second is that of the Eastern Smelting Co.; the third, that of Cornish practice; the fourth, the Penpoll smelter;

the fifth, that of American practice, which involves electrolytic refining, and the sixth, that of the Longhorn tin smelter in Texas,

with dross and secondary material at times. The American practice, however, deals with Bolivian ores, thought of as being the

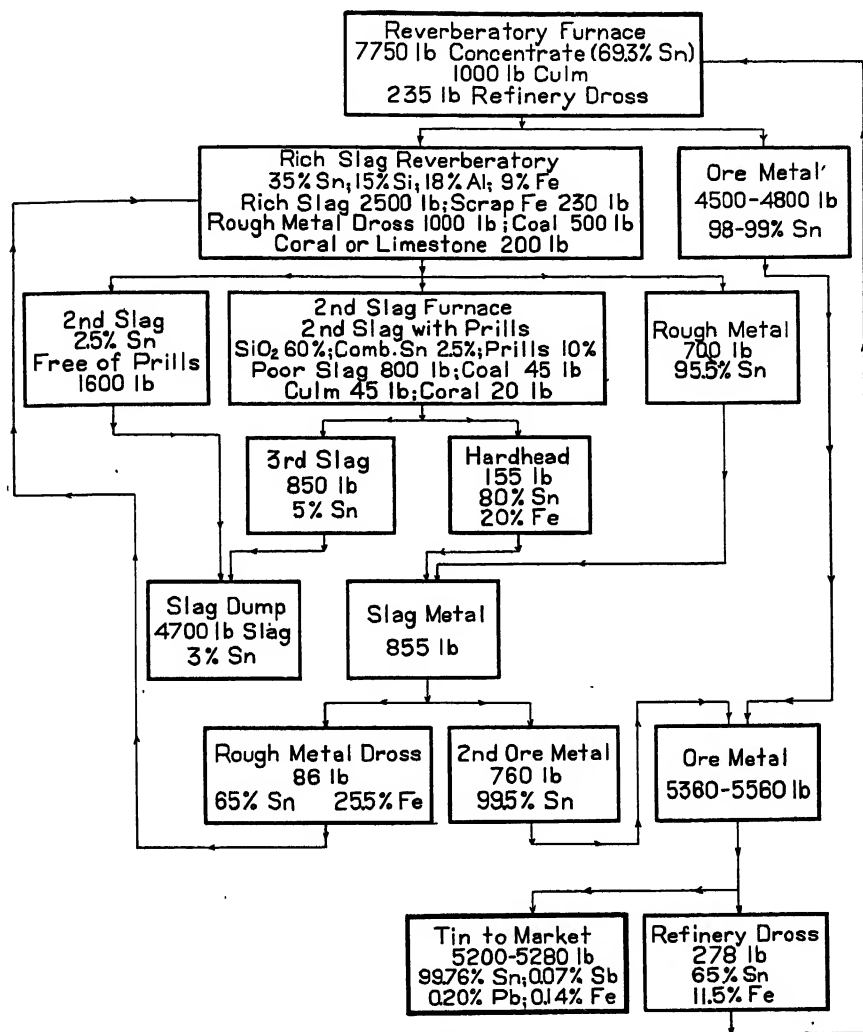


FIG. 1.—FLOWSHEET OF STRAITS PRACTICE.

where acid treatment of ores to prepare them for smelting is an important part of the operation.

It is to be noticed that the first two—that is, Straits Trading and Eastern Smelting—deal with relatively pure ores; the English smelters with pure alluvial ores and mixtures of lode or vein ores, coupled

most difficult to treat because of their complexity and metals other than tin.

TIN SMELTERS

Pulo Brani Works

One of the most eminent smelters in the world is the Pulo Brani Works of the

Straits Trading Co. This plant is on an island off Singapore, Straits Settlements. A process and tonnage flowsheet of the operations is given in Fig. 1. Reverberatory

ing through the furnace bed or through joints drops into the water and is thus granulated, this material being collected periodically. As it is impossible to prevent

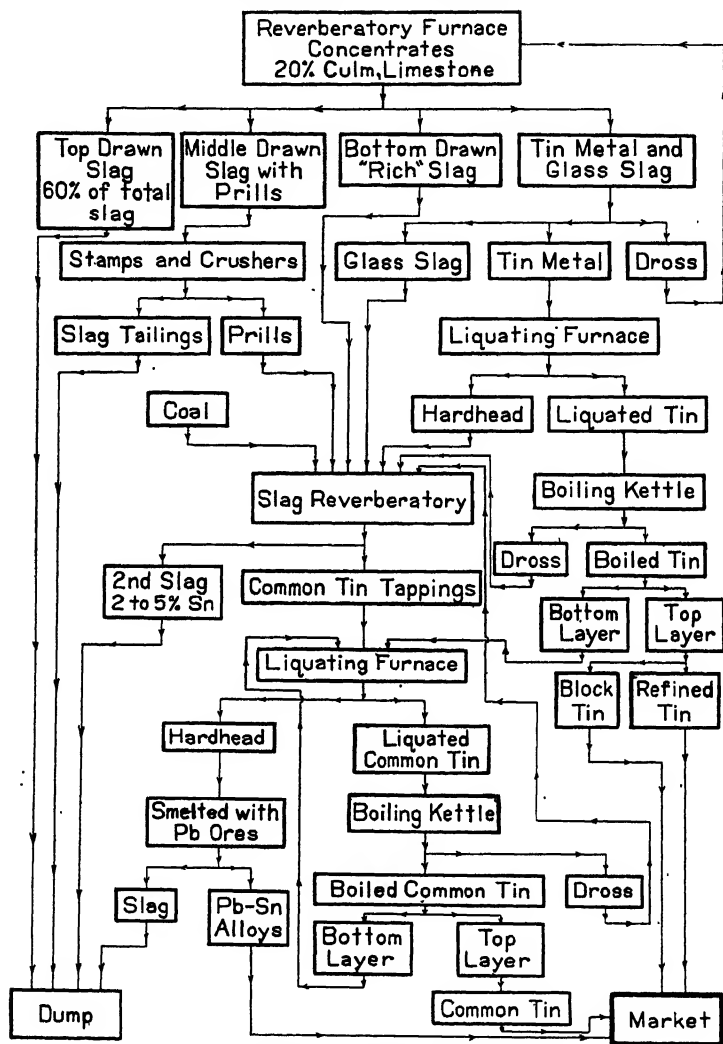


FIG. 2.—FLOWSHEET OF CORNISH PRACTICE.

smelting furnaces are used, a special feature of the furnace being the water vault. The lower part of the furnace foundation, below the ground line, is built so as to form a water tank the full length of the hearth and the length of the holding kettle. An 8-ft. depth of water is maintained. Any tin leak-

leakage of so mobile and easily fusible a metal as tin, this water vault presents to the smelters a satisfactory method of handling leakage and recovering the metal.

Straits practice is summed up in the following operation: Alluvial concentrates are smelted with carbonaceous material to

produce "ore metal" and "rich slag" high in tin. The rich slag is smelted with the aid of coal and scrap iron to produce "rough metal" and "poor slag." The "poor slag"

per cent. Concentrates run from 65 to 70 per cent or better in tin. They are of alluvial or "stream" origin, thus being very pure.



FIG. 3.—TIN-SMELTING REVERBERATORIES AT PENPOLL.
(Courtesy *The Mining Magazine*, London.)

is smelted for prills, producing "hardhead" and another low-grade slag, which is sent to the dump. "Hardhead" and the rough metal, together making the "slag metal," are refined, the dross returning for re-processing, the refined slag metal joining the "ore metal." The total metal recovered from the concentrates is refined by liquation, poling, or tossing. It is stated that in continuous operation 97 to 98 per cent of the metal present in the original concentrates is recovered. The iron consumption amounts to about 5 per cent of the tin produced, and the coal consumption 25 to 30

Penang

The practice of the Eastern Smelting Co. in Penang, Straits Settlement, is described in *The Mining Journal* (London, Jan. 25, 1930) as follows:

On arrival at the works all arsenical and sulphur-bearing ores are first roasted at a low temperature in a large mechanical roasting furnace to eliminate these deleterious impurities. The roasted ore is then sent to the smelting furnaces, together with the clean ores, as received.

The smelting furnaces in use by Eastern Smelting Company, Ltd., are large regenerative

oil-fired reverberatory furnaces. The charge, consisting of ore, clean or roasted, anthracite for reduction, crushed limestone for fluxing purposes and various by-products formed in the smelting operations, passes through the

At intervals the charge is rabbled (stirred) with long-handled iron rabbles.

The reduction of the ore commences in a short time, and tin is drawn off almost continually during the working of the charge.

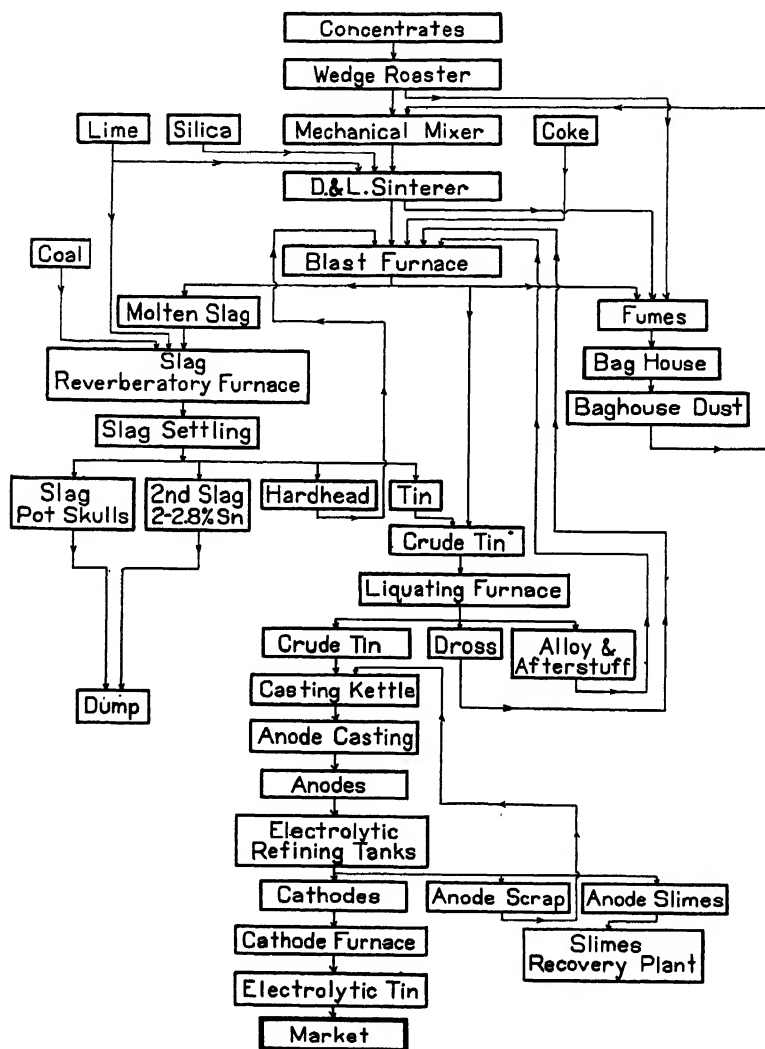


FIG. 4.—FLOW SHEET OF AMERICAN PRACTICE.

charge mixing plant, and is then hoisted to the furnace charging floor, whence it is fed to the furnaces and levelled down. The oil flame is then turned on, and the charge is worked for a period of seven to twelve hours.

At the end of the working period the taphole is opened, and the resultant slag, together with the remaining portion of the reduced tin, is drawn off, the tin into a kettle or a float and the slag into a granulating pit.

The crude furnace tin produced is then sent to the refinery, and the rich slag produced sent to a second slag-smelting furnace. Here the slag is mixed with further anthracite,

products of the slag-smelting furnaces are a rich iron-tin alloy, which is returned to the ore-smelting furnaces, and a slag, low in tin, which is discarded.

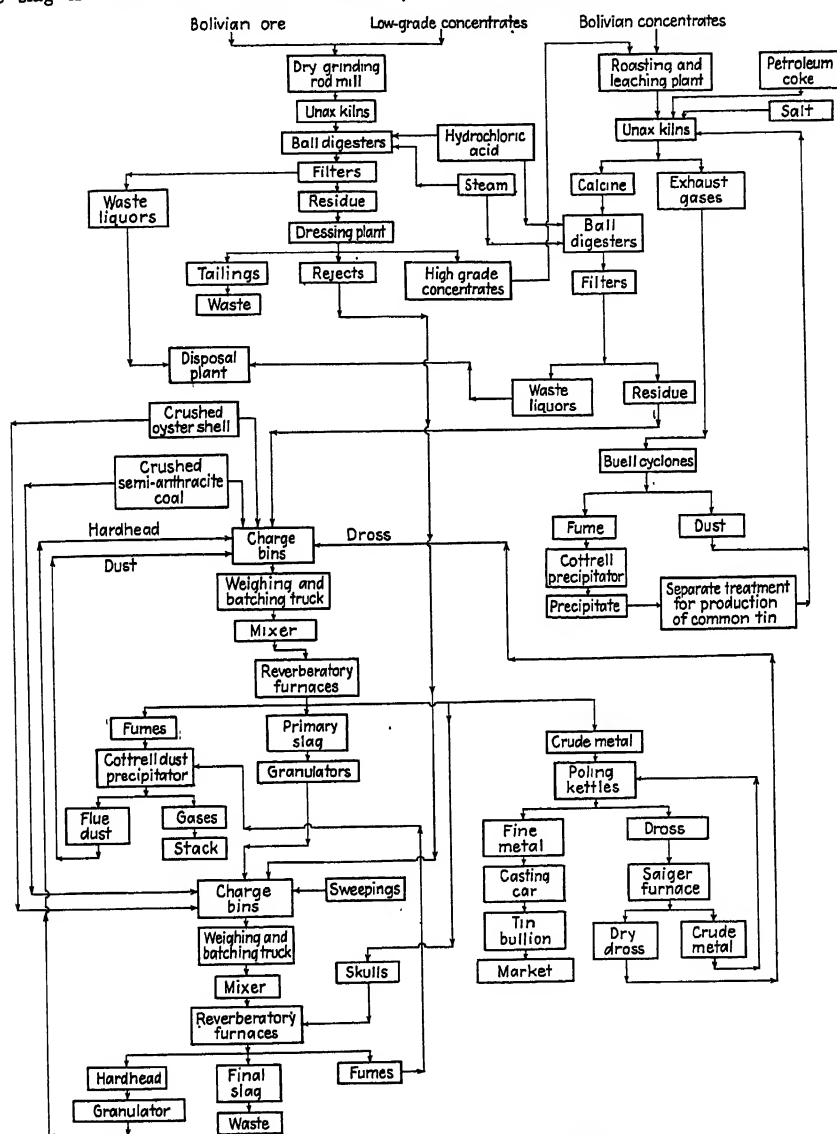


FIG. 5.—FLOWSHEET OF LONGHORN SMELTER.

limestone and occasionally scrap iron and treated similarly to an ore charge, with the exception that no tin is tapped during the working of the charge, the whole of the products being drawn off in the final tapping. The

All furnaces are coupled to a fume and dust collecting plant, which recovers the fine particles of tin and tin oxide carried off with the spent furnaces' gases, the oxide collected being returned to the ore furnaces.

The crude tin drawn off from the furnace is usually impure, and contains different metals—e.g., iron, copper, lead, antimony, arsenic, and bismuth. As these impurities detract from the market value of the tin, it is necessary to remove them by a process of refining, which consists of liquation and “boiling” of the tin. The ingots of crude tin are melted down in a furnace at a low temperature, and the molten tin is allowed to run into a large iron pot or kettle, the less easily fusible metals remaining behind on the bed of the furnace. The tin which collects in the kettle is kept molten during the “boiling” by means of a fire underneath.

The boiling consists of releasing a stream of compressed air from a pipe well below the surface of the molten metal. By this means every portion of the mass of metal is brought into contact with the air, the foreign metals and a portion of the tin being oxidized and collecting as a foamy mass on the surface of the metal. The molten mass is then allowed to stand for some time to allow the heavy impurities to settle to the bottom. After this the scum is skimmed off, and the refined tin poured into molds.

Cornish Practice

Cornish practice is shown in the second flowsheet (Fig. 2). It differs from Straits practice in that ordinarily iron as raw material is not used to replace tin in the slags as a method of recovery. The slags are subdivided to a greater extent and a greater number of varieties of tin are produced. Cornish smelters have to use Bolivian vein ores, diluted with alluvial concentrates. Furnace liquation is used in Cornwall more often in the treatment of the impure tin metal produced. Concentrates are mixed with 15 to 20 per cent of culm, a small amount of lime as a flux, and often some slags, drosses, or other tin-bearing products from other stages of operations. The materials are mixed and dampened before they are charged into the furnace. Furnace temperatures are of the order of 1200° to 1300°C. After rabbling and settling, about two thirds (the upper

two thirds) of the slag is withdrawn and sent to the dump. Another portion is reworked by stamping and crushing for prills. The slag tailings go to the dump, the prills being reworked with the remainder of the slag, which contains appreciable tin in the combined form.

Tin metal from reverberatory smelting is cast into molds, the “glass” slag with it being removed and sent to the slag furnace. The cast tin is liquated, the hardhead going to the slag furnace for reworking. The liquated tin is “boiled” by poling with billets of green wood or admitting air under pressure, and the heavy impurities are allowed to settle out. The top layers of the boiled tin are cast into molds, and, depending upon the purity of the metal, sold as refined tin or as block tin. Drosses return to the concentrate-smelting furnace for reworking; the lower layers from the boiling kettle are mixed with the metal recovered from the slags and other products. The slags containing appreciable tin, the prills, hardhead, and glass slags are treated with some culm in the slag reverberatory. The resultant slags, running from 2 to 5 per cent of tin, are discarded. Metal tappings from the furnaces are cast into molds and sent to the market as common tin. The bottom layers are returned to the slag reverberatory, along with the drosses, for reworking; and the hardhead produced from liquation is either discarded or smelted with antimony or lead ores to produce antimony, tin, or lead-tin alloys, which can be disposed of as such.

Penpoll Smelter

As a modification of the Cornish practice, many mechanical changes and variations were introduced at the Penpoll smelter.

Reverberatory smelting of tin concentrates dates back to the early part of the eighteenth century, when reverberatory furnaces were introduced into Cornwall. They have increased in favor, for they are

adaptable not only for primary smelting but also for slag treatment to recover tin. Reverberatory furnaces produce somewhat cleaner slags in the primary smelting, as

15 to 20 per cent of anthracite screenings, small amounts of slagmaking materials such as sand and limestone, old slag and refinery by-products. Premixing of the

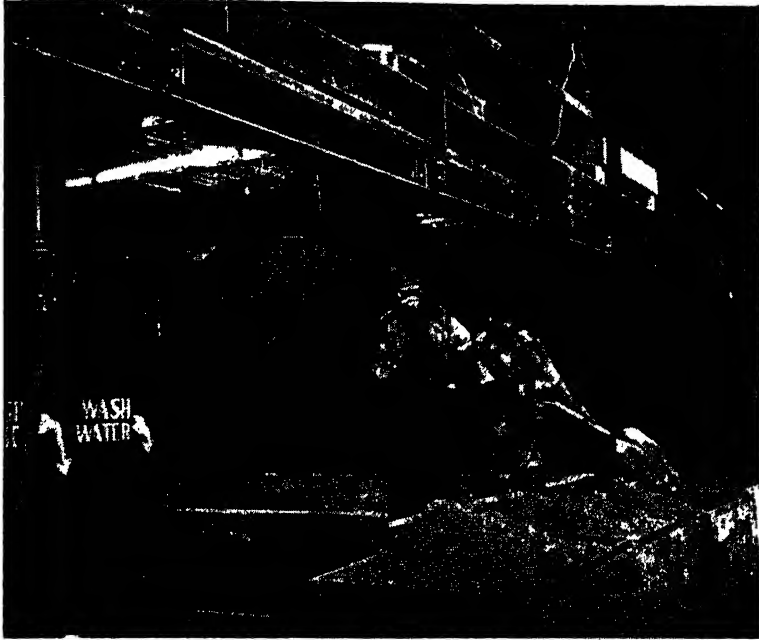


FIG. 6.—DISCHARGING LEACHED ORE FROM BALL DIGESTERS, LONGHORN TIN SMELTER. Courtesy Office of War Information.

well as in the resmelting of the first-run slags. The operations are more readily controlled in reverberatories than in blast furnaces. The reverberatory is particularly suited to the smelting of fine tin ores and concentrates because of the lower dust losses. The furnaces are constructed of firebrick and vary greatly in size. Hearths on the largest ones are approximately 30 ft. long and 12 ft. wide. The firebox is at one end and the flue and stack connection at the other.

Fig. 3 shows one of the most modern tin reverberatories, one of those at the Penpoll smelter at Bootle, England. The fuel is long-flame bituminous coal, although oil is sometimes used. For the larger furnaces, 8 to 12-ton charges are typical. The usual charge consists of tin concentrates with

charge constituents is accomplished usually outside the furnace. The process is entirely a batch operation.

The smelting time of the larger furnaces is usually 10 to 12 hr., at temperatures of 1200° to 1300°C., ordinarily. Relatively large amounts of tin are allowed to go into the slag, as such practice tends toward the production of metal containing a minimum amount of impurities. After the batch is smelted, the practice of handling the fluid slags and tin is the same as in blast-furnace operations. Reverberatory-furnace slags usually run 10 to 25 per cent tin. Rabbling in the furnace is accomplished with iron hoes attached to long iron handles, which are operated through the side doors of the furnace. The stirring is usually done as completely as possible.

Flowsheets

Refining tin by furnace methods is at best an imperfect operation, for large quantities of impurities cannot be sepa-

of raw material at a price that would allow the enterprise to continue. In 1915, tin shortages in the United States and the availability of Bolivian vein ores again



FIG. 7.—TAPPING REVERBERATORY FURNACES AND DISCHARGE OF LIQUID TIN INTO "SETTLERS," LONGHORN TIN SMELTER.

Courtesy Office of War Information.

rated. The quality of the metal produced depends very largely on the original purity of the concentrates.

American tin-smelting practice, when plants existed in the United States for the treatment of foreign tin ores, was more advanced than any others so far developed. In 1903, R. T. White, built a plant for the International Tin Co. at Bayonne, N. J., to smelt Straits of Malacca (Malayan) concentrates. The British Government then placed a 40 per cent ad valorem export duty on tin ores to other than British smelters, so the plant failed, owing to lack

made possible the establishment of tin smelters.

The flowsheet of the Maurer plant of the American Smelting and Refining Co. is given in Fig. 4. This plant treated Bolivian ores exclusively. The material termed "ore" is a concentrate containing between 55 and 65 per cent of tin, with arsenic, antimony, iron, copper, tungsten, bismuth, lead, and sulphur as impurities. The ore was given a preliminary roast in a Wedge furnace, to drive off sulphur by oxidation and antimony and arsenic by volatilization. The ore from the Wedge furnace was

mixed with blast-furnace dust (recovered in the baghouse) in a mechanical mixer. It passed on to a Dwight and Lloyd sintering machine, where it was sintered with

and 38 to 40 per cent lime, magnesia, and alumina. An average slag in good tin-smelting practice was about 33 per cent silica, 28 per cent iron oxide, and 28 per



FIG. 8.—POLING KETTLES FOR TREATMENT OF CRUDE METAL FROM REVERBERATORY FURNACES, LONGHORN TIN SMELTER.
Courtesy Office of War Information.

lime and sometimes silica. Lime was added to the sinter charge to protect the grate bars of the machine and also for fluxing the sulphur remaining in the ore. The sintered ore passed to the blast furnace, where it met drosses from various operations, coke, and the fluxes or slag-forming materials.

Special care had to be taken in proportioning the slag to prevent it from being too basic, as under such condition the tin compounds in the ore formed stannates and were lost in the slag; and not too acid, because under that condition tin silicates formed and were similarly lost.

The best proportions of the slag components were found to be 38 to 40 per cent silica, 22 to 28 per cent iron oxide (FeO),

cent lime. Finished slags were of about the percentage composition: SiO_2 , 35; FeO, 18; CaO, 28; Sn, 2.8 to 2.5; and the remainder, MgO and Al_2O_3 .

Very good slags, metallurgically speaking, were 3:4 sesquisilicates.

In the blast furnace the stannous oxide, when produced, acted as a basic constituent, whereas the stannic oxide acted as an acid one. It is interesting to note at this point that the stannous sulphide was volatile at 1075°C ., whereas the temperature of the blast might go as high as 1400°C .

In practically all plants the first slag produced from the blast furnace contains such large quantities of tin that it must be re-treated practically as if it were an origi-

nal ore. At the Maurer (New Jersey) plant it was claimed, however, that better than 90 per cent of the tin in the original ore was

casting kettle for casting into anodes. The slag from the reverberatory, containing 2.0 to 2.8 per cent tin, was sent to the dump.



FIG. 9.—CASTING PURE TIN INTO BLOCKS OR BARS, LONGHORN TIN SMELTER.
Courtesy Office of War Information.

recovered and that there was little volatilization of tin compounds.

In the Maurer flowsheet, the blast furnace produced a crude tin, which went to the liquating furnace, and a high-tin slag, running 6 to 10 per cent tin, which was sent in the molten condition to the slag reverberatory. Fumes from the blast furnace were collected in the baghouse, returning to the process by mixing and sintering with fresh ore. The slag, at $1100^{\circ}\text{C}.$, was raised to about 1300° in the slag reverberatory and treated with lime and coal. It was then settled. Tin metal produced was either sent to the liquating furnace, joining the tin from the blast furnace, or placed in the

Slag-pot skulls went to waste. Iron-tin alloy or hardhead was returned to the blast furnace.

The crude tin from the blast furnace was liquated and then cast into anodes on a continuous anode-casting wheel. Dross, alloy, and scrap returned to the blast furnace. The anodes were sent to the electrolytic refinery and refined in a manner almost identical with that for copper, using lead-lined tanks and a sulphate-fluosilicate electrolyte. The product, ready for market, was 99.8 per cent tin.

The anode slime, which, in the refining, in contradistinction to copper refining, clings to the anodes, was washed from the

anode scrap and worked up for bismuth, and in some cases for arsenic, antimony, lead, and other constituents. Anode scrap was returned to the anode furnace for re-casting into anodes.

Electrolytic tin is lower in impurities than any of the foreign brands of tin. It is claimed that an average of three fourths of a ton of slag was produced per ton of 60 per cent concentrates smelted. The tin loss in slags was 1.5 to 2.5 per cent of the tin. Electrolytic refining losses were 10 lb. per ton of 97 per cent tin anodes refined. Tin recoveries were of the order of 94 to 97 per cent of the metal originally charged as concentrates.

The Longhorn tin smelter, in Texas, operates a processing method on Bolivian ores which is in many ways a modification of that used by the Billiton Company at the Arnhem smelter in Holland.

As described by the plant management, the process used is as follows:¹⁰

The Longhorn smelter is constructed for handling all grades of tin compounds from the pure alluvial concentrates to the lowest grades of primary ores, and the treatment process depends upon chemical composition and physical properties. For the pure alluvial ores, which contain only small amounts of silica and iron and traces of other metallic impurities, a simple two-step reduction process in reverberatory furnaces is adequate to yield a high-grade metal at a high recovery. The greater part of the primary ores and concentrates from Bolivia contain, however, base metals in such quantities that reverberatory smelting would yield a low-grade metal whose use would be limited. In addition to the base metals such as arsenic, antimony, copper, lead, and bismuth, these ores contain excessive sulphur, which must be eliminated before reverberatory smelting can be used. The iron content is often too high for direct smelting, and in the low grades of Bolivian ores the percentage of silica is also high.

(The complexity of the flowsheet is illustrated in Fig. 5.)

Upon arrival, the ore is weighed, sampled, and stored in piles according to the required treatment. Most of the ore comes under the classification in which the silica content is less than 10 per cent. It is calcined, with or without the addition of a reducing agent or common salt, the iron and other impurities thus becoming readily soluble in hot hydrochloric acid. The calcining is carried out in Unax kilns. These special kilns are provided with water-cooled cylinders in which the hot calcined ore is cooled to room temperature, with the exclusion of air to prevent reoxidation.

The extreme fineness of the ore causes dust losses in the kilns; most of this dust is precipitated in Buell cyclones directly connected with the kilns, and the precipitate is immediately returned to the kilns. The cooled gas is further treated in a Cottrell installation, where the remaining dust is precipitated together with the fumes. The precipitate from this installation runs high in antimony and arsenic, so is treated separately. The calcined material from the kilns is leached in digesters with hot hydrochloric acid. These are of spherical design and have a rubber lining protected from heat and abrasion by two layers of acidproof brick. Steam, necessary to ensure the desired leaching temperature, is supplied through one of the hollow trunnions. The spheres rotate slowly, so that the ore is agitated continuously, and a high elimination of impurities is obtained. Leaching time depends upon the amount of impurities and varies between 4 and 8 hr. The capacity of the digesters depends upon the specific gravity and the iron content of the ores treated and ranges between 8 and 11 tons per batch.

Leaching is followed by filtering of the chloride solution on Nutsch filters. After having been washed with diluted acid, the residues are of such purity that subsequent treatment in reverberatory furnaces will yield a metal of at least 99.80 per cent tin.

Medium and low-grade ores received generally contain excessive amounts of gangue and iron compounds. They can be divided into two groups. In the first, the percentage of base metals is so low that direct smelting will yield a hardhead from which pure metal may be produced. The gangue and iron compounds are carried off in the slag together with a small amount of tin. The other group, in which

TABLE I.—*Analyses of Typical Tins*
PER CENT

Kind or Source of Tin	Tin	Anti- mony	Arsenic	Lead	Bis- muth	Copper	Iron	Silver	Sulphur	Cobalt	Nickel and Cobalt	Cad- mium	Zinc
Union Minière du Haut Katanga.....	99.966	0.002	0.006	0.012	tr.	0.013	0.003	nil	tr.				
American electrolytic tin.....	99.928	0.007	0.012	nil	0.012	0.018	0.015	nil	tr.				
Banka.....	99.950	0.006	nil	nil	nil	0.023	tr.	nil	tr.				
Billion.....	99.960	tr.	0.013	tr.	nil	0.023	0.003	nil	0.005				
Penang.....	99.939	0.008	0.045	0.034	0.003	0.056	0.003	0.006					
Singapore.....	99.970	0.015	0.015	0.042	0.001	0.017	0.003						
Mt. Bischoff.....	99.847	0.015	0.015	0.042	0.001	0.017	0.003	tr.	0.008				
Pyrmont.....	99.795	0.015	0.015	0.037	0.005	0.035	0.004	tr.	0.004				
Irvine Bank.....	99.938	0.017	0.019	tr.	nil	0.024	0.002	nil	0.004				
McAlister, Lamb and Flag.....	99.586	0.002	0.034	0.221	0.025	0.126	0.002	0.018	0.004				
Williams, Harvey and Co.: No. 1.....	99.190	0.100	0.000	0.100	0.350	0.000	0.020						
No. 2.....	99.860	0.015	0.040	0.004	0.005	0.047	0.003	nil	0.006				
No. 3.....	99.500	0.100	0.037	0.102	0.007	0.050	0.005	tr.	0.013				
No. 2-a.....	99.350	0.245	0.005	0.223	0.015	0.042	0.016	tr.	0.013				
No. 3.....	99.200	0.300	0.037	0.396	0.007	0.100	0.013	0.014	0.005				
No. 4.....	99.941	0.011	0.022	0.396	0.001	0.020	tr.	0.005					
Reduth.....	99.160	0.176	0.053	0.177	0.017	0.445	0.041	0.016	0.008	0.012			
O. T. Lempriere and Co.....	99.180	0.011	0.016	0.019	0.012	0.026	0.020	0.017	0.008	0.008			
Cornish refined.....	99.880	0.012	0.006	0.014	tr.	0.046	0.003	0.017					
Cornish Lamb and Flag.....	99.321	0.174	0.034	0.068	tr.	0.205	0.040	0.044	0.047				
German Lamb and Flag.....	99.080	0.150	0.080	0.500	0.000	0.080	0.050	0.044					
Th. Gutschmidt: No. 1.....	99.860	0.004	nil	0.102	nil	0.043	tr.	nil	tr.				
No. 2.....	99.400	0.015	nil	0.435	nil	0.069	tr.	nil	tr.				
No. 3.....	99.150	0.122	0.046	0.143	0.112	0.352	0.007	0.006	tr.				
T. Sutton and Sons.....	99.550	tr.	0.022	0.342	0.015	0.045	0.010	tr.	0.011	0.072			
Chinese No. 1.....	99.343	0.031	0.040	0.434	0.007	0.052	0.010	tr.	0.011				
Wing, Hong and Co.: No. 1.....	99.343	0.031	0.040	0.434	0.007	0.052	0.010	tr.	0.011	0.072			
No. 2.....	98.662	0.039	0.035	1.035	0.012	0.134	0.014	tr.	0.011	0.058			
No. 3.....	95.286	0.381	0.050	3.995	0.020	0.160	0.020	0.018	0.008				
Vulcan electrolytic.....	99.958	0.008	tr.	tr.	0.002	0.004	0.003	0.001					
Vulcan American refined.....	99.997	0.0012	tr.	0.0021	incl. with lead	0.0099	0.0048	0.0001					
Metal and Thermit Corp. electrolytic.....	99.971	0.005	tr.	0.012	0.001	0.001	0.011						
Tin Processing Corp. Govt. smelter at Texas City Three Star Long Horn.....	99.880	0.037	0.02	0.20	0.004	0.025	0.004	0.0005	0.005	0.005	0.005	tr.	tr.
U.S.A. Bids (Max.) 5-14 Dec. 1939.....	99.8	.04	0.05	0.05	0.015	0.04	0.015	0.001	tr.	0.001	0.001		
Murex refined.....	99.895	.020	0.023	0.036	0.006	0.012	0.008	0.009	0.007				
Fenpoll No. 1.....	99.720	0.118	0.054	0.041	0.007	0.052	0.004	0.015	0.004				
No. 2.....	98.710	0.569	0.042	0.546	0.055	0.103	0.007	0.021	0.009				
No. 3.....	99.300	0.325	0.056	0.212	0.050	0.088	0.002	tr.					
Special refined.....	99.9309	0.019	tr.	0.0256	0.0015	0.0102	0.0087	0.009	0.007	0.0041			
Refined.....	99.800	0.118	0.054	0.041	0.007	0.032	0.004	0.009	0.007	inl			tr.
Capper Pass Chempur.....	99.9946	tr.	tr.	tr.	tr.	0.0038	0.0016	nil	0.0002				
Capper Pass Chempur.....	99.9918	0.0031	nil	0.0025	0.0004	0.0004	0.0016	0.00025	0.00025				
Capper Pass Chempur No. 1.....	99.9895	0.0035	0.001	0.0008	0.0001	0.0005	0.0025	0.0005	0.00025				

metallic impurities are too high, will not yield a clean hardhead by smelting, so a roasting and leaching process, as already described, has to be used first. Generally these ores become free-milling after this treatment, so that the residues yield high-grade concentrates on jigs and tables in the dressing plant.

If the dressing-plant concentrates still contain excessive amounts of base metals, they are retreated in the roasting and leaching plant, yielding a high-grade residue, ready for smelting. The tailing of the dressing plant can sometimes be discarded directly, but usually it pays to recover the tin by smelting to a final slag with a low tin content and a hardhead from which common tin can be recovered.

Smelting of all concentrates and clean residues is done in two steps in reverberatories fired with natural gas. In the first step, known as ore smelting, the amount of reducing agent is limited, so that metallic tin practically free of iron is obtained. After this operation, the slag still carries considerable tin. In the second operation, the primary slag is further reduced to a low tin content in the final slag. To obtain the desired results, a great amount of iron is reduced simultaneously, forming an alloy with the tin, called hardhead. This hardhead, usually containing over 80 per cent tin, is treated simultaneously with the ore in the first operation, whereby the iron acts as a reducing agent.

The metal produced from the primary smelting is tapped in floats and transported to poling kettles in which the metal is refined by means of steam. After stirring and skimming, it is ready for casting. A certain amount of the tin volatilizes and is carried with the exhaust gases to the Cottrell installation, where it is precipitated and from which it is returned into the reverberatory furnaces.

Tin's high price and scarcity warranted the construction of an extensive dust-precipitation

plant, from which the recovery will be better than 99 per cent. Further tin losses appear in slags containing about one per cent tin. In the leaching process, a small percentage of the tin is converted into tin chloride, which currently is not recovered, though treatment of the waste solution, by which the metallic impurities and tin will be precipitated, is contemplated.

Some of the operations at the newest tin smelter in the world are shown in Figs. 6 to 9.

As an indication of the quality of the product from all the tin mines, reduction works, smelters, and refineries in the world, a table of typical tin analyses is given (Table 1), which is a composite of data collected from a large number of different sources.

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